EFFICIENCY OF VARIOUS CORROSION INHIBITORS TO RESIST CARBONATION AND CHLORIDE INDUCED CORROSION

A dissertation submitted in the partial fulfilment of the requirements for the award of degree of

MASTERS OF ENGINEERING

IN

STRUCTURAL ENGINEERING

Submitted By:

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DECLARATION

I, Aditya Rana, hereby declare that this dissertation entitled **"EFFIECIENCY OF VARIOUS CORROSION INHIBITORS TO RESIST CARBONATION AND CHLORIDE INDUCED CORROSION"** in fulfilment of the requirement for the award of Degree of Master of Engineering in Structural Engineering at Thapar University, Patiala, is an authentic record of my work carried out during a period from January 2017 to July 2017 under the supervision of **Dr. Shweta Goyal, Associate Professor,** Department of Civil Engineering, Thapar University, Patiala.

This matter presented in this dissertation has not been submitted by me for the award of any other degree of this or any other University.

Date: 30th July, 2017.

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CERTIFICATE

This is to certify that above statement made by the student concerned is correct and true to the best of my knowledge and belief.

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ABSTRACT

Concrete is the second most used material by humans after water. Concrete may be considered as best construction material but its durability can adversely be effected by various means. Corrosion of steel present in reinforced concrete is most significant durability problem in the world of civil engineering. Concrete structures in coastal areas and aggressive environments are constantly exposed to these corrosive substances. Out of those substances, chlorides and CO_2 are the most dominating. These can cause reduction in strength, spalling, expansion or mass loss in concrete. Hence, many methods have been developed to reduce or prevent corrosion of steel in concrete. From all the methods available for corrosion protection, corrosion inhibitors sound very promising.

Inhibitors that are available in market usually have a tendency to protect against only one factor of corrosion i.e. either carbonation or chlorides along with the fact that commercially available corrosion inhibitors are very expensive and affect the total cost of structure. Due to which, there arises a need to find a cheaper replacement which can inhibit corrosion due to carbonation and presence chlorides.

In this study of finding more effective inhibitors, effectiveness of some commonly available cheap chemicals is evaluated. Corrosion inhibition of Picolinic Acid, 4-Aminobenzoic acid, Salicylaldehyde and 2-Aminopyridine with 1% addition is assessed. Fe 500 HYSD steel bars of 12 mm diameter and 60 mm length are being prepared and then submerged partially in six different solutions for different time periods with a maximum of 480 hours. Corrosion monitoring of these steel bars is performed at 1 hour, 24 hours, 48 hours, 120 hours, 240 hours and 480 hours of immersion. The amount of resistance to corrosion provided by respective inhibitor is obtained by two tests i.e. Half-Cell Potential and Linear Polarization Resistance sweep tests.

It has been observed that all of the chemicals used as corrosion inhibitors, have successfully inhibited corrosion, and were able to form a passive layer which protected the steel surface from further corrosion.

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CHAPTER 1 INTRODUCTION

1.1 GENERAL

Reinforced concrete is an important construction material due to its compression and tension taking capability, and is used for almost all types of construction purposes for its proved durability and high structural performance. The durability of concrete structures and their long-term performance have emerged over the last few decades as a primary concern for structural engineers, infrastructure owners, and consumers. However, problems may start to occur within only a few years, not because of a structural problem, but because of a durability issue. The deterioration of a concrete structure may occur due to many processes, which act individually or combined. Some examples of processes that cause material deterioration include alkali aggregate reactivity, sulphate attack, freezing and thawing, and corrosion of reinforcement inside the concrete.

1.2 CORROSION OF RC STRUCTURES

Corrosion of reinforcing steel bars (rebars) inside concrete is one of the major reason that reduce the service life of a concrete structure, and it imposes an extra load on the maintenance budget of the affected structure. Corrosion of reinforcement in concrete is an electrochemical process, once initiated, corrosion products which are having higher volume than that of the parent metal around 3-6 times *(V Kumar et al., 2013*), will accumulate in the space between the rebar and concrete, and since there is almost no space in concrete to accommodate these products, cracking and spalling of the concrete cover will surely occur. If the rebar cross sectional loss is severe, structural problems may start to occur.

Figure 1.1 shows an example of concrete cover spalling due to the corrosion of the reinforcing steel bars of a beam that supports a bridge superstructure. This sight, although may not be structurally dangerous, is a source of concern to the public. Thus, a repairing process is required in order to maintain structural safety.

Figure 1.1 Corrosion of a cross girder that supports the main bridge deck *(www.concretebridgesview.com)*

Therefore corrosion control of steel reinforcement is a subject of paramount importance. Corrosion is a form of damage which is often stealthy and hidden until striking at the worst moment of a system operation. As explained above, the corrosion product generally occupies 3-6 *(V Kumar et al., 2013*) times more volume as compared to parental material. As a result, the corrosion products produces an internal stress that destroys the neighbouring concrete under tensile stress.

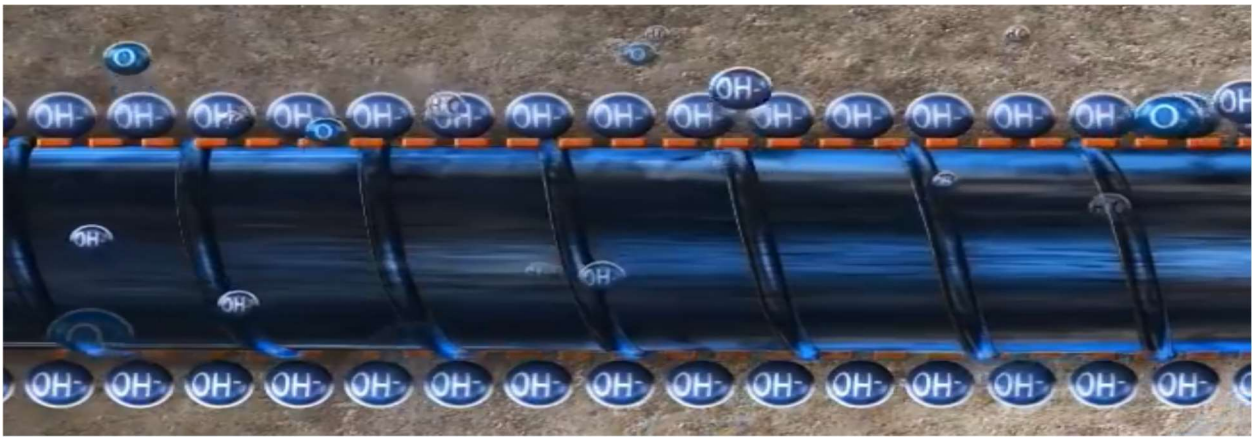


Figure 1.2 Layer of $Fe(OH)_3$ film formed around Steel bar *(http://chemblinks.blogspot.in)*

As will be discussed later, there are two main causes for steel corrosion in concrete: carbonation or chloride ion attack.

The first one occurs when the atmospheric carbon dioxide reacts with concrete alkalis, causing a drop in the pH of the concrete pore solution, which reduces its ability to protect steel from corrosion *(Broomfield, 1997)*. The second one occurs when chloride ions diffuse through the concrete cover and attacks the reinforcement directly, inducing very high corrosion rates *(Broomfield, 1997)*. The use of de-icing salts, chloride-contaminated aggregates and the exposure to seawater are the main sources for chloride ions in concrete.

The prevention and treatment of rebar corrosion can be done by several techniques which include, increased cover over the rebars, reduced water cement ratios, denser concretes, latex or polymer modified concrete overlays, waterproofing membrane with asphalt overlays, epoxy coated rebars and cathodic protections are used. Use of epoxy coated rebars was initially believed to be ideal solution to prevent corrosion of rebars, but its long term effectiveness is being questioned.

1.3 MECHANISM OF CORROSION

The process of steel corrosion inside concrete is defined as the removal of iron atoms (Fe) from steel and their dissolution in the surrounding water solution, appearing as ferrous ions (Fe^{+2}) *(Monticelli et al., 2000)*. Because of this dissolution, steel loses mass, and its cross section becomes smaller. Rust is a result of the corrosion process. For this process to occur, moisture and oxygen must be present, and both of them are available in concrete. However, due to the high alkalinity inside concrete (pH > 12), steel will be able to form a very thin film (~ 10 nm (0.01 μm)) called the passivation layer *(Monticelli et al., 2000)*, which acts as a protective coating that prevents the metal from taking part in the corrosion process. Unfortunately, this layer can be disrupted due to either carbonation or chloride ion attack. The chemical reactions are similar for both of them.

The corrosion process actually involves two separate, but coupled, electrochemical reactions that take place simultaneously at two different sites on the steel surface *(Broomfield, 1997)*. These two chemical reactions are known as the anodic and cathodic reactions. The areas on which they occur in the steel are called anodic and cathodic areas or simply anode and cathode. The two reactions are as follows:

Anodic reaction

$Fe \rightarrow Fe^{+2} + 2e^{-}$ Metallic atoms ions dissolved at the steel surface in the solution

Cathodic reaction

$\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2(OH)^-$ Dissolved oxygen Dissolved ions molecules in the solution

The anodic and cathodic reactions are only the first step in the process of creating rust. Several more stages must occur for rust to form:

$Fe+2 + 2OH- \rightarrow Fe(OH)_2$

Ferrous hydroxide

$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$

Ferric hydroxide

$2Fe(OH)_3 \rightarrow Fe_2O_3.H_2O + 2H_2O$

Hydrated ferric oxide (rust)

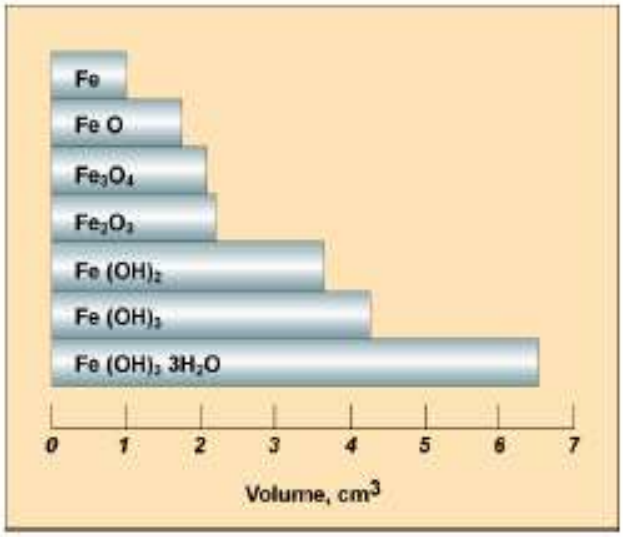


Figure 1.3 Relative volume of Corrosion product with respect to Iron (*www.theconcreteportal.com*)

The hydrated ferric oxide has a volume of three to six times that of the original volume of steel *(V Kumar et al., 2013*) and since there is not enough space at the concrete-steel interface, these products will accumulate and cause tension stresses on the concrete cover. Eventually, these stresses will exceed the concrete tensile strength causing cracking and spalling of the concrete cover. Figure 1.4 shows a schematic diagram for the process of steel corrosion inside concrete.

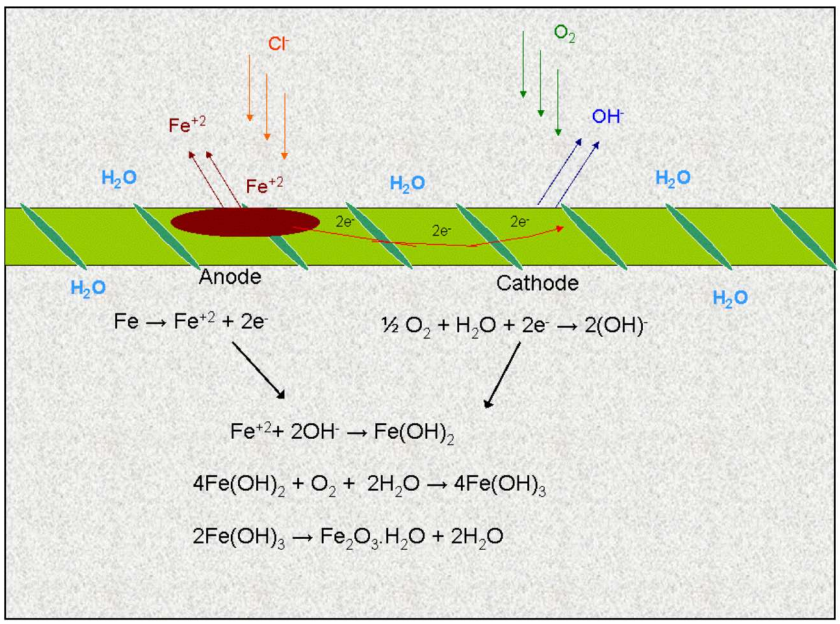


Figure 1.4 Schematic diagram for the process of steel corrosion in concrete *(Bruno Huet et al., 2002)*

1.4 CAUSES OF CORROSION OF STEEL

1.4.1 Carbonation

Carbonation is a result of the interaction of carbon dioxide gas in the atmosphere with the alkaline hydroxides in the concrete. Due to the high alkalinity of the concrete pore water, the steel reinforcing bars are passivated by an iron film (Fe_2O_3) that protects the steel. At this pH value a passivated film forms on the steel that reduces the rate of corrosion to a very low and harmless value.

Figure 1.5 gives an idea about the pH values according to steel corrosion occurrence in concrete. This figure also helps in getting an idea about the pH required for breaking of passive layer around steel surface, which protects steel from further corrosion.

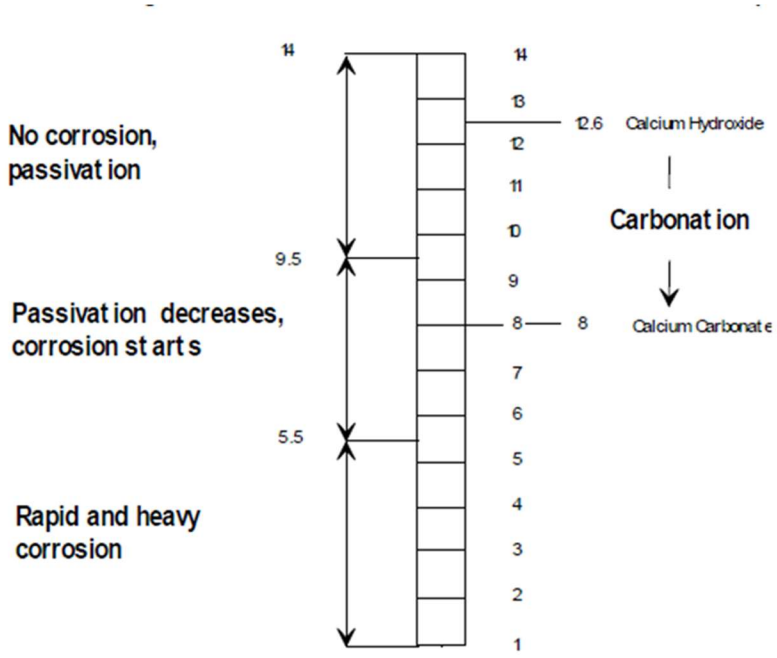


Figure 1.5 pH values according to steel corrosion occurrence

Concrete is permeable and allows the slow ingress of the atmosphere, the acidic gas react with the alkalis (using Calcium, Sodium and Potassium hydroxides), neutralizing them by forming carbonates and sulphates, and at the same time reducing the pH value. If the carbonated front penetrates sufficiently deeply into the concrete to intersect with the concrete reinforcement interface, protection is lost and, since both moisture and oxygen are available, the steel is likely to be corroded. The extent of the advance of the carbonation front depends to a considerable extent, on the porosity and permeability of the concrete and on the conditions of exposure.

In the case of carbonation, atmospheric carbon dioxide (CO_2) diffuses through concrete and reacts with pore water alkalis according to the following reactions;

$CO_2 + H_2O \rightarrow H_2CO_3$

$Ca(OH)_2 + H_2CO_3 \rightarrow CaCO_3 + 2H_2O$

This consumes reserve alkalinity and reduces the pH of the pore water to the range of 8 to 9, where carbon steel is no longer passive (i.e. the passivation layer will vanish), and then it will start to corrode. In other words, carbonation causes deterioration of the passive layer by reducing the concentration of the OH^- ions in the concrete pore water. Thin concrete cover and poor concrete quality increases the risk of carbonation.

1.4.2 Chloride induced corrosion

An important basis for durability design of concrete structures is chloride ingress, which is a common cause for concrete deterioration. Chloride ions from de-icing salts are the primary cause of reinforcement corrosion in infrastructural structures the steel passive layer in concrete can be disrupted due to the presence of chloride ions that accumulate on the rebar surface until they reach a certain concentration; afterwards, the passivation layer is disrupted. The source of chloride ions could be either external (by using de-icing salts or from seawater in marine environments) or internal (by using contaminated aggregate or using concrete admixtures 10 that contain chloride). This kind of de-passivation is local and is accompanied by a type of corrosion called pitting corrosion. On the contrary, the de-passivation by carbonation is general and uniform corrosion will occur on the entire rebar surface.

The concentration of chloride ions required to initiate rebar corrosion is called the chloride threshold level (CTL). Chloride threshold level can be expressed either as a percentage of total or free chloride content per cement weight or as a ratio between the concentrations of chloride ion and hydroxyl ion dissolved in the concrete pore water (Cl^-/OH^-). Fig 1.6 Illustrates the process of chloride induced corrosion in reinforced concrete.

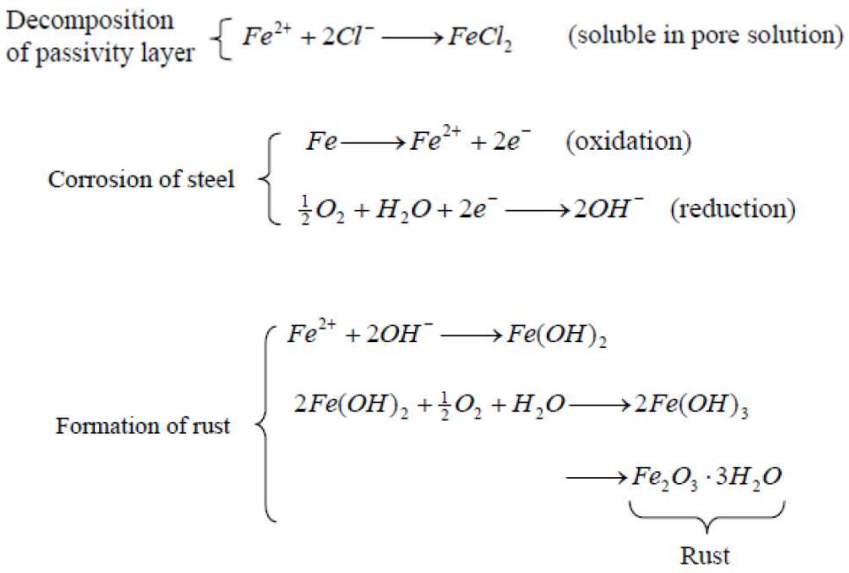


Figure 1.6 Illustrates the process of chloride induced corrosion in reinforced concrete (*hongten91.wordpress.net)*

Steel embedded in hydrating concrete reacts with oxygen to form a thin (~10 nm thick) layer of insoluble ferrous oxide on its surface (so called passivity layer). This layer strongly adheres to the underlying steel and prevents it from any further corrosion as long as the alkalinity of environment remains high (pH>12). Chloride ions, however, react with the ferrous oxide and form a soluble complex which dissolves in the surrounding solution and does not provide any longer protection. The chemical reactions involved are shown in Figure in 1.6.

For corrosion process to continue, the presence of oxygen and moisture are necessary. There will be limited corrosion in dry concrete (i.e. when the relative humidity inside concrete is less than 60 percent), and also in concrete fully immersed in water (due to the lack of oxygen). The relative humidity that is most susceptible for corrosion is between 70 and 80 percent *(Neville 1996)*.

1.5 CLASSIFICATION OF CORROSION

There is no universally accepted classification for corrosion, but the following classification is adapted:

1.5.1 Uniform or general corrosion

Uniform or general corrosion, as the name imply, results in a fairly uniform penetration (or thinning) over the complete exposed metal surface. The general attack results from local corrosion cell action, that is, multiple anodes and cathodes are operating on the metal surface at any given time. The place of the anodic and cathodic areas continues to move about on the surface, ensuing uniform corrosion. In this case the exposed metal/alloy surface area is entirely corroded in an environment such as a liquid electrolyte (chemical solution, liquid -metal), gaseous electrolyte (air, CO_2, SO_2 etc.) or a hybrid electrolyte (solid, water, biological organisms, etc.). Figure 1.7 shows a storage container corroded uniformly under atmospheric conditions.

Figure 1.7 Container corroded uniformly *(http://chemblinks.blogspot.in)*

1.5.2 Galvanic corrosion

Galvanic corrosion is an electrochemical action of two different metals in the company of an electrolyte and an electron conductive path. It occurs when dissimilar metals are electrically coupled in a common solution, the more negative (more active) metal will be the anode of the galvanic corrosion cell and its corrosion rate will increase.

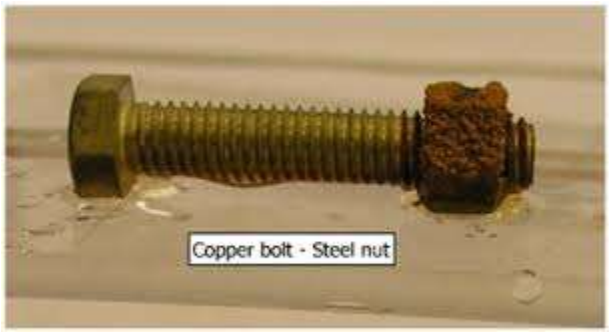


Figure 1.8 Example of Galvanic corrosion ***(http://www.tecnoconverting.com)***

1.5.3 Localized corrosion

This term implies that, specific parts of an exposed surface area corrode in a suitable electrolyte. This form of corrosion is more difficult to manage than the general corrosion. Localized corrosion can be classified as:

1. **Crevice corrosion:** Crevice Corrosion refers to the localized attack on a metal surface at, or immediately adjacent to, the gap or crevice between two joining surfaces. The gap or crevice can be formed between two metals or a metal and non-metallic material. It is similar to pitting corrosion in a stagnant electrolyte after its initiation. This form of corrosion starts due to changes in local chemistry such as reduction of oxygen in the crevice, increase in pH with increasing hydrogen ion concentration and boost of chloride ions. Oxygen depletion implies that, cathodic reaction for oxygen reduction cannot be sustained within the crevice area and consequently metal dissolution occurs. It is frequently more intense in chloride environments. The mechanism of crevice corrosion is electrochemical in nature and it is illustrated in Fig. 1.9. It requires a prolong time to start the metal oxidation process, but it may get accelerated afterwards.

Figure 1.9 Crevice corrosion on a stainless steel flange exposed to a chloride-rich medium. ***(http://www.cdcorrosion.com)***

2. **Filiform corrosion:** Filiform corrosion is a special form of corrosion that occurs under some thin coatings in the form of randomly distributed threadlike filaments. Filiform corrosion is also known as "under film Corrosion" or "filamentary corrosion". Filiform corrosion of a tin-coated steel. Lacquers and "quick-dry" paints are most susceptible to the problem. Their use should be avoided except absence of an adverse effect has been established by field experience.

Figure 1.10 Fillform Corrosion ***(http://www.cdcorrosion.com)***

3. **Pitting corrosion:** Pitting Corrosion is "self-nucleating" crevice corrosion, starting at occluded cells. Corrosion products frequently cover the pits, and might form "chimneys". Pitting is considered to be more risky than uniform corrosion damage because it is more complex to detect, predict and prevent. Large crevices are less expected to corrode because water movement causes mixing and replenishes oxygen, hydrogen ions, bicarbonate or hydrogen sulphide.

Figure 1.11 Pitting corrosion on Steel rebars.

4. **Intergranular corrosion:** Intergranular corrosion is a localized type of corrosion. It is a preferential attack on the grain boundary phases or the zones directly adjacent to them. Little or no attack is experienced on the main body of the grain. This results in the loss of strength and ductility. The attack is often fast, penetrating severely into the metal and causing failure.

1.5.4 Microbiologically influenced corrosion (MIC)

MIC refers to corrosion that is affected by the presence and activities of microorganisms (bacteria, fungi etc.) and/or their metabolites. An aerobic bacterium produces highly corrosive species as part of their metabolism. Most materials, including metals, polymers, glass and ceramics can be degraded in this manner. The production of corrosive species such as minerals, organic acids, ammonia, sulphide and the various types of microbes tend to act synergistically in the corrosion of materials with their interactions typically being of a complex nature.

1.5.5 Erosion corrosion

The term “erosion” applies to deterioration due to mechanical force. When the factors contributing to erosion accelerate the rate of corrosion of a metal, the attack is called “erosion corrosion”. It is the result of a combination of an aggressive chemical environment and high fluid surface velocities. This can be the result of fast fluid flow past a stationary object, such as the case with the oilfield check valve, or it can result from the quick motion of an object in a stationary fluid, such as when a ship's propeller churns the ocean. Surfaces which have undergone erosion corrosion are generally fairly clean, unlike the surfaces from many other forms of corrosion.

1.6 METHODS TO INHIBIT CORROSION

Various Physical, Chemical and Electrochemical repair techniques are available today, to arrest rebar corrosion and hence extend the service life of reinforced concrete structures. Physical techniques are generally used for repair works, while the chemical techniques can be used in the new structures. Electrochemical Techniques work by applying on an external anode and passing the current from it to steel so that all of the steel is made into a cathode.

There are several methods of corrosion protection, such as, but not limited to, the following:

- The use of membrane-type coatings applied to the surface of concrete structures
- Painting the outer concrete surface to provide barrier protection
- Addition of corrosion inhibitors to concrete
- The use of stainless steel or 3CR12 as a substitute for normal carbon steel reinforcement
- Cathodic protection of the reinforcement.
- Application of a coating to the reinforcement itself, i.e. epoxy coatings and specifically zinc in the form of hot dip galvanizing.
- Adequate thickness of concrete cover to isolate reinforcing steel from ingress of deleterious chemicals.
- Avoidance of chloride-containing admixtures.

In last quarter century, many methods have been developed to reduce or prevent corrosion of steel in concrete. From all the methods available for corrosion protection, corrosion inhibitors sound very promising.

1.7 THESIS OUTLINE

This thesis consists of five chapters, plus references and appendices.

Chapter 1 presents an introduction to the mechanism and remedial measures which can be used to resist corrosion in reinforced concrete steel.

Chapter 2 provides the necessary knowledge about the inhibitors and the way they work.

Chapter 3 provides a literature review on the process of steel corrosion inside concrete and synthetic pore solutions simulating concrete, and its causes. The electrochemical techniques that are used in this study to characterize the corrosion of samples, and an overview on the research done by others regarding the corrosion behaviour of carbon steel in concrete and solutions simulating concrete.

Chapter 4 describes the composition of the solutions and materials used, sample size and shape, sample preparation and testing procedure.

Chapter 5 presents the test results and a detailed discussion of these results, including a comparison between corrosion rates on steel bars under investigation.

Chapter 6 presents the conclusions of the study.

CHAPTER 2 CORROSION INHIBITORS

2.1 INTRODUCTION

Corrosion Inhibitor is define as ‘‘a chemical substance that decreases the corrosion rate when present in the corrosion system at suitable concentration, without significantly changing the concentration of any other corrosion agent’’ *(ISO 8044 1989*). This definition excludes other corrosion protection methods such as coatings, pore blockers and other materials, which change the water, oxygen and chloride concentrations. However, some inhibitors also behave as pore blockers, which is a secondary property**.**

Corrosion inhibitors may be a good alternative to other protection methods or classical repair methods due to its lower cost and easy application.

2.2 USE OF CORROSION INHIBITOR IN CONCRETE

Corrosion inhibitors are chemical admixtures which are generally added to cement concrete mixes during batching or are applied on the surface of concrete after casting, usually in very small concentration. Corrosion inhibitors are a practical corrosion-protection measure for the long-term durability of both conventionally reinforced and pre-stressed concrete structures. When used as part of a multiple-strategy corrosion-protection system, they are promising materials to delay the onset of reinforcing and pre-stressing steel corrosion.

Inhibitors are often used in combination with low-permeability concrete and usually they have the effect of increasing the threshold chloride concentration needed to initiate corrosion. Inhibitors play an important role in protecting uncoated high-strength steel strands used in pre-stressed concrete bridge members and stays used in cable-stayed bridges. They are also used in cementitious grouts for filling the ducts of bonded post-tensioned bridges. Inhibitors may also reduce the subsequent corrosion rate after the initiation of corrosion, which ultimately leads to less corrosion-induced concrete deterioration.

There are three major concerns regarding the use of corrosion inhibitors.

- Long-term stability and performance of the inhibitor.
- The inhibitor’s effect on corrosion propagation after corrosion initiation.
- Inhibitor’s effect on the concrete’s physical properties over the service life of the structure.

In order for a corrosion inhibitor to be an effective long-term corrosion-protection measure, it needs to be:

- Able to maintain long-term stability.
- It should be chemically intact and physically present (not leaching or evaporating) to retain its effectiveness.

Inhibitors may have an effect on the corrosion process after corrosion initiation. An insufficient dosage will have a negative impact on corrosion progression. Some inhibitors will have an effect on chloride transport and can reduce the rate of chloride ion migration.

Inhibitors should not have any negative effects on the concrete properties. The use of an inhibitor should not cause an undue increase in the amount of any concrete cracking. Some inhibitors decrease the concrete resistivity, which has a tendency to increase the corrosion rate. This effect is offset due to the inhibition provided by a suitable corrosion inhibitor.

The efficiency of an inhibitor can be expressed by a measure of this improvement:

$$\text{Inhibitor efficiency (\%)} = 100\ \frac{[\text{CR(uninhibited)} - \text{CR(inhibited)}]}{\text{CR(uninhibited)}}$$

Where CR (uninhibited) = corrosion rate of the uninhibited system,

CR (inhibited) = corrosion rate of the inhibited system.

The scientific and technical corrosion literature has descriptions and lists of numerous chemical compounds that exhibit inhibitive properties. Of these, only very few are actually used in practice. This is partly because the desirable properties of an inhibitor usually extend beyond those simply related to metal protection. Considerations of cost, toxicity, availability, and environmental friendliness are of considerable importance.

2.3 CLASSIFICATION

2.3.1 On the basis of physical mode of application inhibitor can be classified into 2 groups:

I. Admixed inhibitor

II. Migrating inhibitor

I. Admixed inhibitors: Those compounds which are added to the fresh concrete at the time of mixing for new structures are known as admixed inhibitors *Jamil et al. (2005)*. Admixed inhibitors are commercially available since 1960's. These compounds are added immediately after the addition of water to cement. Admixed inhibitor influence initial set, later strength gain or other properties i.e. hydration processes of cement. To overcome this, retarder was added to concrete mix which balances the acceleration of the inhibitors and provided a little more retardation.

The inorganic compounds which are based upon calcium nitrite sodium nitrite, sodium benzoate and sodium chromate are used as admixed inhibitors. Organic compounds based upon mixtures of alkanol amines, amines or amino-acids, or based on an emulsion of unsaturated fatty acid ester of an aliphatic carboxylic acid and a saturated fatty acid also proposed as a admixed inhibitors.

II. Migrating inhibitors: These are the chemical which are applied on the hardened concrete surface and are able to diffuse through concrete to the underlying rebar where they act to suppress both the anodic and cathodic corrosion reactions by forming a monolayer film at the steel-concrete interface *Soylev et al. (2008).* According to physical mode of application these types of inhibitors are also known as Surface applied corrosion inhibitors or Penetrating corrosion inhibitors. Use of migrating corrosion inhibitors are proposed in the last 15-20 years and are generally proposed for the repair works.

These inhibitors are typically based either on mixtures of alkanol amines and amines or on inorganic compounds based upon Monofluro-phosphate. In addition, nitrite ions can penetrate into concrete by absorption and diffusion if applied to the surface by spraying or ponding with aqueous solutions. Alkanol amines and amines have relatively high vapour pressure under atmospheric conditions, assisting diffusion and migration into concrete. Amino alcohols, such as ethanolamine and dimethyl ethanolamine, can act at the cathode and prevent oxygen reduction to hydroxyl ion by a blocking mechanism, following adsorption on the steel surface.

2.3.2 Based upon the mechanisms of protection

2.3.2.1 Anodic inhibitors

Anodic inhibitors usually act by forming a protective oxide film on the surface of the metal causing a large anodic shift of the corrosion potential. This shift forces the metallic surface into the passivation region. They are also sometimes referred to as passivators. Chromates, nitrates, tungstate, molybdates are some examples of anodic inhibitors.

2.3.2.2 Cathodic inhibitors

Cathodic inhibitors act by either slowing the cathodic reaction itself or selectively precipitating on cathodic areas to limit the diffusion of reducing species to the surface. The rates of the cathodic reactions can be reduced by the use of cathodic poisons. However, cathodic poisons can also increase the susceptibility of a metal to hydrogen induced cracking since hydrogen can also be absorbed by the metal during aqueous corrosion or cathodic charging. The corrosion rates can also be reduced by the use of oxygen scavengers that react with dissolved oxygen. Sulfite and bisulfite ions are examples of oxygen scavengers that can combine with oxygen to form sulfate.

2.3.2.3 Mixed Inhibitors

Mixed inhibitors work by reducing both the cathodic and anodic reactions. They are typically film forming compounds that cause the formation of precipitates on the surface blocking both anodic and cathodic sites indirectly. Hard water that is high in calcium and magnesium is less corrosive than soft water because of the tendency of the salts in the hard water to precipitate on the surface of the metal forming a protective film. The most common inhibitors of this category are the silicates and the phosphates. Sodium silicate, for example, is used in many domestic water softeners to prevent the occurrence of rust water. In aerated hot water systems, sodium silicate protects steel, copper and brass. However, protection is not always reliable and depends heavily on pH. Phosphates also require oxygen for effective inhibition. Silicates and phosphates do not afford the degree of protection provided by chromates and nitrites, however, they are very useful in situations where non-toxic additives are required.

2.3.2.4 Volatile inhibitors

Volatile corrosion inhibitors (VCIs) also called vapour phase inhibitors (VPIs) are compounds transferred in a closed environment to the site of corrosion by volatilization from a source. In

boilers, volatile basic compounds such as morpholine or hydrazine are transported with steam to prevent corrosion in condenser tubes by neutralizing the acidic carbon dioxide or by shifting the surface pH towards less acidic. If the corrosion product is volatile, it volatilizes as soon as it is formed, thereby leaving the underlying metal surface exposed for further attack. This causes rapid and continuous corrosion leading to excessive corrosion. For example, molybdenum oxide (MoO_3), the oxidation corrosion product of molybdenum is volatile. In closed vapour process (shipping containers), volatile solids such as salts of dicyclohexylamine, cyclohexylamine and hex methylene amine are used as volatile corrosion inhibitors.

2.4 APPLICATION OF CORROSION INHIBITORS

Corrosion inhibitor can be used for various purposes. It can be used as following:

- Can be added to fresh concrete as an admixture.
- Applied on the hardened concrete surface, so called penetrating corrosion inhibitor (also migrating corrosion inhibitor and surface-applied corrosion inhibitor).
- Be added to repair mortars.
- Used as a surface treatment on the reinforcement bars before concreting.
- Volatile amines are used in boilers to minimize the effects of acid. In some cases, the amines form a protective film on the steel surface and, at the same time, act as an anodic inhibitor. An inhibitor that acts both in a cathodic and anodic manner is termed as mixed inhibitor. Figure 2.1 shows application of surface corrosion inhibitors.

Inhibitors used in cases of pitting corrosion can act:

- By film forming prior to the ingress of chlorides.
- By buffering the pH in the local pit environment.
- By competitive surface adsorption process between inhibitor and chloride ions.
- By competitive migration of inhibitor and chloride ions into the pit.

Figure 2.1 Application of surface inhibitor *(http://www.tecnoconverting.com)*

3.1 GENERAL

The problems of corrosion of steel in concrete still exist despite the extensive research conducted over the last 20 years. The numerous factors involved in this type of corrosion instigate a number of studies to help understand the phenomenon and an equal number to bring about its prevention.

3.2 EFFECT OF CORROSION INHIBITORS IN RESISTING CORROSION OF REBARS

Literature from previous researches shows that use of corrosion inhibitors is an effective method for preventing the corrosion of steel in concrete. The following studies shows that use of corrosion inhibitors in pore solution simulating the environment of freshly prepared concrete and in concrete mix reduces the rebar corrosion**.**

M. Moreno et al. (2004)

They investigated the effects of the chloride concentration on both the polarization characteristics and the corrosion rate of as received reinforcing steel immersed in solutions simulating the pore liquid of alkaline and carbonated concrete, with particular reference to the critical chloride concentration. The electrochemical processes affecting rebar corrosion in concrete were analysed by means of potentiodynamic polarization curves. The corrosion rate of steel was monitored in time by means of polarization resistance measurements. The effect of different levels of carbonate plus bicarbonate in the simulated pore solution was also evaluated.

For saturated $Ca(OH)_2$ (pH=12.5) + x% Cl^- (x = 0 to 0.2) solutions.. The instantaneous corrosion rate diminished during the exposition, reaching a value lower than 10^{-7} A/cm^2.

Also in this media the corresponding penetration rate was 1lmm/year. In the chloride containing solutions, at concentrations equal to or higher than 0.02% (0.056 M) the Icorr raised to values more than one order of magnitude above that found in the absence of chlorides.

Figure 3.1 shows the potentiodynamic anodic polarization curve for carbon steel in saturated Ca(OH)2 solution, pH=12.5, containing different concentrations of chloride ion. Figure 3.2 shows the development of the corrosion potential for carbon steel during a one-week exposure in a saturated Ca(OH)2 solution, pH=12.5, containing different concentrations of chloride ion.

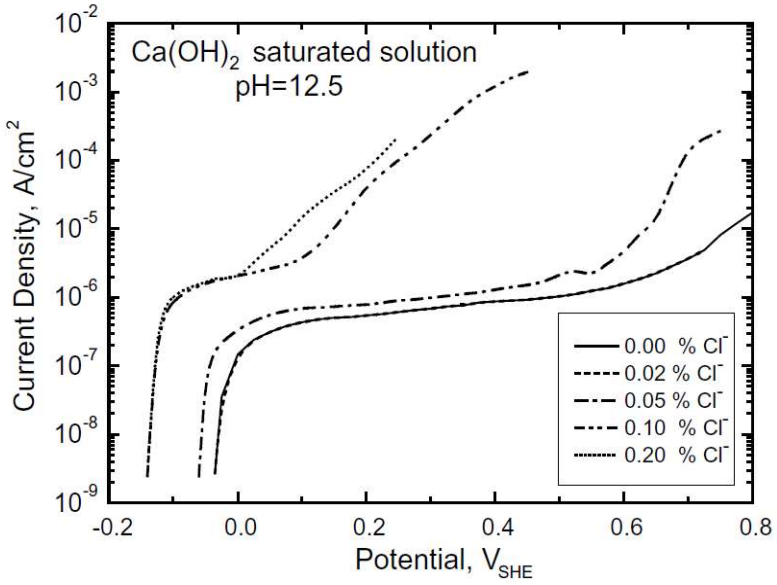


Fig. 3.1 Potentiodynamic anodic polarization curve for carbon steel in saturated $Ca(OH)_2$ solution, pH=12.5, containing different concentrations of chloride ion. (*M. Moreno et al. (2004)*)

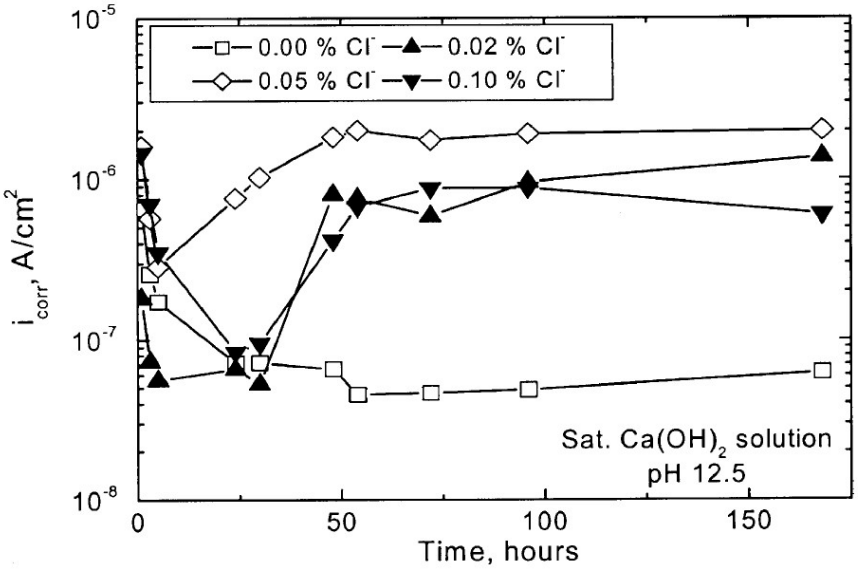


Figure 3.2 Development of the corrosion potential for carbon steel during a one-week exposure in a saturated $Ca(OH)_2$ solution, pH=12.5, containing different concentrations of chloride ion. *(M. Moreno et al. (2004)*)

Rong Liu et al. (2014)

Their study included two different kinds of simulated concrete pore solutions: the $Ca(OH)_2$ + KOH + NaOH solution and the cement extract. Compared with the familiar $Ca(OH)_2$ + KOH + NaOH solution, the cement extract represents the real environment of the concrete pore solution due to the hydration action of the cement. This study was conducted to examine the effect of the carbonation on chloride-induced reinforcement corrosion in the simulated concrete pore solutions.

The corrosion monitoring of the steel was based on the open-circuit potential (Ecorr) and the corrosion current density (Icorr), which was calculated by electrochemical impedance spectroscopy (EIS).

A cylindrical steel specimen with a diameter of 1 cm and length of 3 cm was used. A copper wire was welded to one end surface of the steel specimen and the other end surface was used to test in the electrochemical methods. The flank and the end surface with a thick copper wire were sealed with the help of epoxy resin. The tested surface was polished with SiC water polishing papers. The cement extract was made by dissolving 20 g cement powder in 2 L distilled water.

The cement used in this study was No. 42.5 ordinary Portland cement made in China. Varying concentrations of sodium bicarbonate were added to the exposure solutions to produce different levels of carbonation, which systematically assess the effect of carbonation on chloride-induced reinforcement corrosion. The aggressive chloride ions were supplied by sodium chloride and added 0.01 mol/L every 2 days. All chemical reagents used in this work were of analytical grade reagents and experimental water was deionized water.

A classical 3-electrode device system was employed: the steel bar was a working electrode, while a saturated calomel electrode and a platinum electrode were joined to work as a reference and auxiliary electrode, respectively.

Table 3.1 presents the composition and pH of the simulated concrete pore solutions which were used for the experimental purpose.

Table 3.1 Composition and pH of the simulated concrete pore solutions.

SOLUTION	COMPOSITION	pH
1	$Ca(OH)_2$ + KOH + NaOH	13.12
2	$Ca(OH)_2$ + KOH + NaOH + 0.02M $NaHCO_3$	12.71
3	$Ca(OH)_2$ + KOH + NaOH + 0.2M $NaHCO_3$	9.46
4	Cement extract (w/c = 10:1)	12.95
5	Cement extract (w/c = 10:1) + 0.02M $NaHCO_3$	12.59
6	Cement extract (w/c = 10:1) + 0.2M $NaHCO_3$	9.43

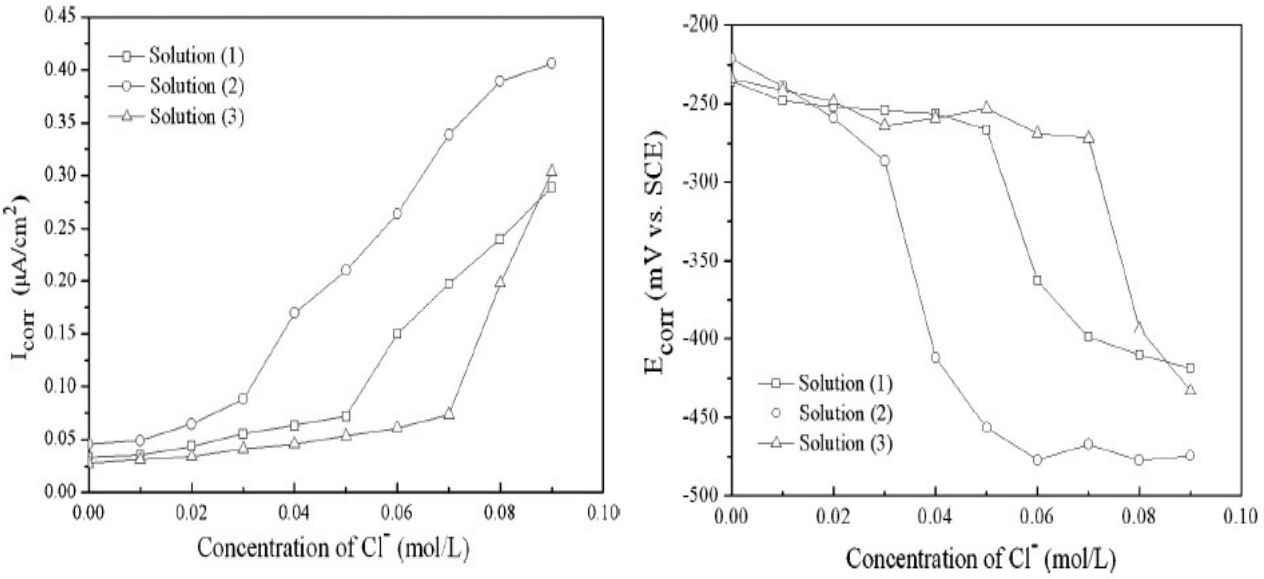


Figure 3.3 Variations of the Icorr and E_{corr} for the specimens in solutions (1–3) with the concentrations of chloride ions *(Rong Liu et al. (2014)*

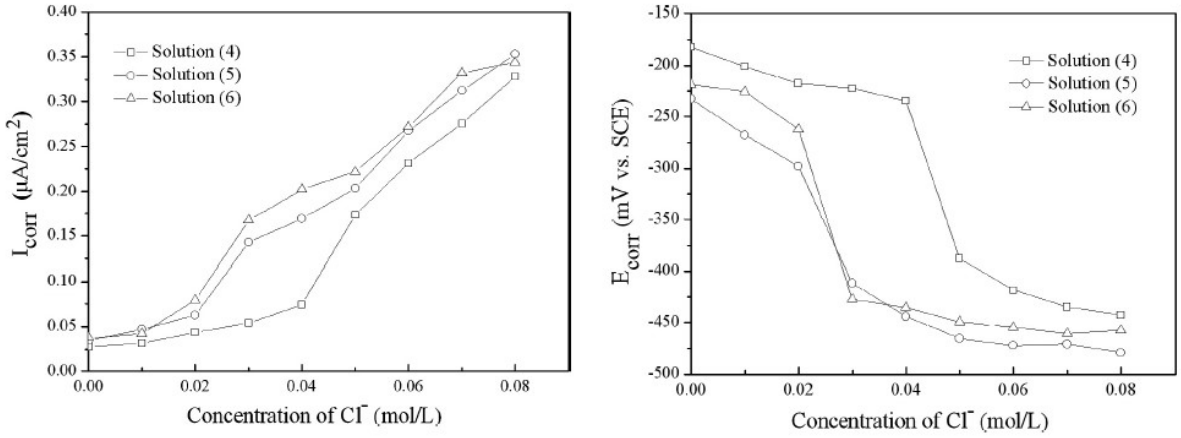


Figure 3.4 Variations of the Ecorr and Icorr for the specimens in solutions (4–6) with the concentrations of chloride ions. (Rong Liu et al. (2014)

Figure 3.3 and 3.4 results shows that the corrosion resistance to chloride ion of the steel in concrete is affected by the degree of carbonation: high concentrations of bicarbonate lower the danger of chloride-induced corrosion of the steel, but quite on the contrary, the steels under the condition of low HCO_3 concentrations are more likely to corrosion.

Fig 3.4 give the evolutions of the Ecorr and Icorr. for the specimens immersed in solutions (4–6) with the concentrations of chloride ions, respectively. The initial E_{corr} for the steel specimens in a passive state are relatively higher (less negative), and the corresponding Icorr. are quite low. With the more level of chloride ions, the Ecorr reduce and Icorr. increase by degrees. Then, when a certain concentration of chloride ions is added, a sudden shift of Ecorr and Icorr. appear, the value of E_{corr} decreases to more negative and the value of Icorr. increases to much higher. The fact is related to the rupture of the passive film caused by the aggressive chloride ions.

The addition of bicarbonate ions decreases the chloride level needed for the active corrosion and increases the corrosion susceptibility of the steel specimens, which is disagree with the results obtained from the $Ca(OH)_2$ + KOH + NaOH solution. The reason for the different results is mainly own to the difference between the two kinds of simulated solutions. The hydration products of OPC such as C–S–H gel and CH can interact with the bicarbonate and chloride ions. The chloride ions can be physical absorbed to the C–S–H gel and react with the unhydrated C_3A to form the Friedel's salt. Meanwhile, the bicarbonate ions will react with CH and the C–S–H gel to form solid products and the concentrations of the soluble bicarbonate ions are very low hence, the solution

(6) shortens the time needed for the onset of pitting corrosion because of the low soluble bicarbonate ions, although the initial addition of bicarbonate ions in solution (6) is very high. In the $Ca(OH)_2$ + KOH + NaOH solution, the effect of bicarbonate ions on the corrosion behavior of the steel specimens depends on the concentration of bicarbonate ions.

A high HCO_3^- concentration will enhance the stability of the passive film and the corrosion resistance of the steel specimen, while the low concentration of HCO_3^- ions accelerates the corrosion. However, no agreement on the effect of HCO_3^- ions has been obtained in the cement extract. The added HCO_3^- ions in the cement extract plays a role in promoting the corrosion initiation because of the low concentration of the soluble HCO_3^- ions.

Jang et al. (1995)

They investigated corrosion of reinforcing steel (rebar) samples in concrete saturated solutions containing corrosion-inhibitor-added de-icing salts and salt substitutes as well as in plain sodium chloride solutions. Galvanic cells were used to determine the effects of corrosion-inhibitor-added de-icing salts and salt substitutes on rebar corrosion.

The reinforcing steel samples were galvanically coupled and were recovered after 240 days. Pit depths and area percentages of corrosion were determined on the reinforcing steels with an optical microscope. Optimum concentrations were found to exist for the corrosion-inhibitor added de-icing salts and salt substitutes in reducing the rebar corrosion. Dramatic changes of pH values were noted in the concrete-saturated solutions containing corrosion-inhibitor added de-icing salts and salt substitutes.

The formation of precipitates caused by chemical reactions between a concrete- saturated solution and corrosion-inhibitor-added de-icing salts and salt substitutes was observed, also there is an optimum concentration of the corrosion inhibitor- added de-icing salts and salt substitutes for effective reduction of rebar corrosion. And was also noted that rebar corrosion due to corrosion-inhibitor-added de-icing salts and salt substitutes is generally less than 50% of that resulting from plain NaCI solutions.

Tommaselli et al. (2009)

They studied the effectiveness of corrosion inhibitors in saturated calcium hydroxide solutions acidified by acid rain components. They analysed the effect of sodium nitrite and sodium

molybdate as corrosion inhibitors in a saturated calcium hydroxide solution polluted with sulfuric and nitric acids (acid atmosphere) using Anodic Polarization curve and Impedance test. Both compounds showed significant inhibitory effects depending on the concentration. sodium molybdate showed an efficiency of approximately 67% whereas sodium nitrite showed an efficiency of 52% at low concentrations that is 0.013% total solution mass, but at 0.040% total solution mass (at high concentrations) their inhibitory effect was found to be similar. Figure 3.5 shows the potentiodynamic anodic polarization curve for steel in saturated Ca(OH)2 solution, pH 12.5 and pH 8 containing different concentrations of sodium nitrite.

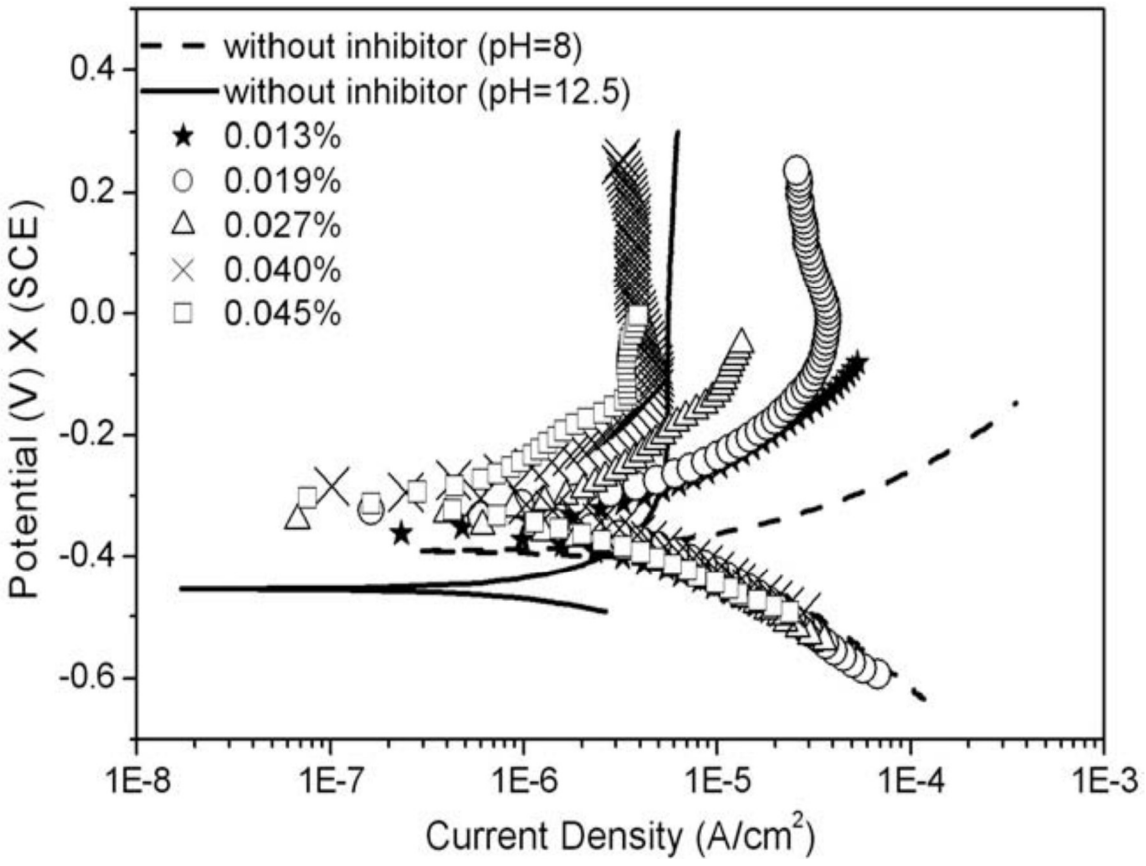


Figure 3.5 Potentiodynamic anodic polarization curve for steel in saturated $Ca(OH)_2$ solution, pH 12.5 and pH 8 containing different concentrations of sodium nitrite ***(Tommaselli et al. 2009)***

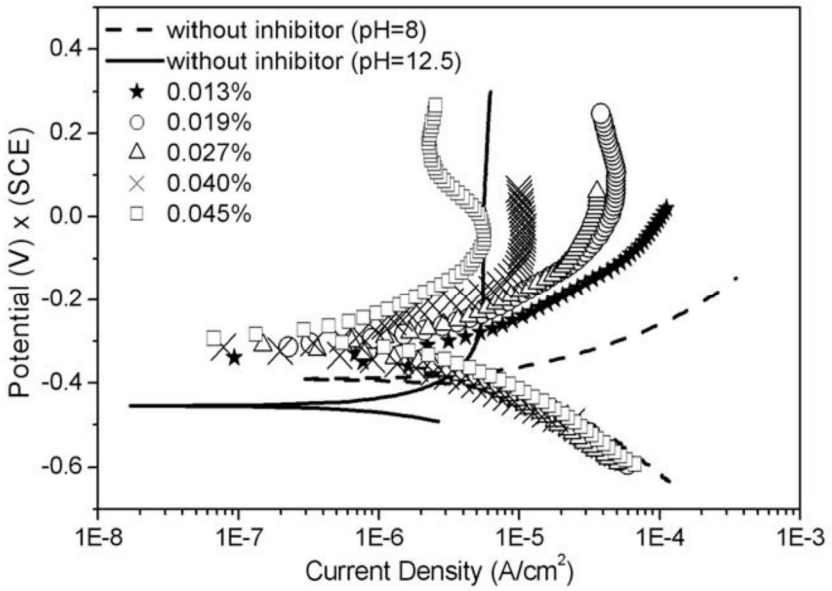


Figure 3.6 Potentiodynamic anodic polarization curve for steel in saturated $Ca(OH)_2$ solution, pH 12.5 and pH 8 containing different concentrations of sodium molybdate. ***(Tommaselli et al. 2009)***

Huet et al. (2005)

They aimed to investigate the transition from passive to active corrosion of mild steel rebars in carbonated concrete. For this purpose electrochemical techniques (polarization curves, free corrosion potential measurements) and surface analyses (EDS, XRD, XPS) were used. Five different electrolytes, with pH ranging from 13 to 8.3, were chosen to simulate the interstitial concrete pore water at various degrees of carbonation. The results indicate that the transition pH is between 10 and 9.4.

XPS results indicate a passivation of mild steel for pH values ranging from 13 to 10 due to the formation of a thin iron III oxide layer. Immersion tests highlight the importance of the buffering effect of the 25 carbonate content. At the free corrosion potential in an aerated solution, a decrease of the carbonate content increases the corrosion rate. On the opposite, at low electrode potential, the kinetics of oxidation increases with the carbonate content. Passivation of Fe500 steel from pH 13 to 10 is confirmed by an increase of Ecorr during corrosion test. After immersion, XPS analyses have shown that the oxide layer formed is very thin (<10 nm) and is mainly composed of iron III oxides. Decreasing the pH and/or decreasing the carbonate content of the electrolyte promotes the

active corrosion of mild steel sample leading to the formation of a large amount of iron oxides that do not protect the steel substrate from further corrosion.

Królikowski and Kuziak (2011)

They took steel electrodes that were made of structural carbon steel rods with 8 mm diameter and about 19 cm^2 surface area exposed to the solution. The steel surface was polished with emery paper from 120 to 220 grit and then degreased with acetone and rinsed with methanol. Here inhibition effect of calcium nitrite was performed in a solution that represented the pore liquid in chloride contaminated concrete. The test protocol was adjusted to follow the performance of penetrating corrosion inhibitors in real reinforced concrete structure.

First the steel samples were pre-passivated by exposure to saturated solution of $Ca(OH)_2$ for 3 days. It was noted that at least 2 days exposure in alkaline solution was necessary to reach a good passive state of carbon steel. Then the steel was exposed to the solution as chloride contaminated concrete that is saturated solution of $Ca(OH)_2$ with addition of 1% NaCl. The steel samples were kept in this solution for 7 days to initiate corrosion. Subsequently, doses of calcium nitrite were added to simulate a gradual increase in the inhibitor concentration thus corresponding decrease in the chloride to nitrite ratio. All solutions were prepared from analytical grade reagents using double-distilled water. Calcium nitrite was supplied as 30% aqueous solution. Solutions were open to air and kept at room temperature (20±2 ˚C) during the test.

Two series of test were performed with different manner of calcium nitrite addition. Larger doses of inhibitor were given in the series CA I, so the final value of this ratio equal 0.33 was reached after 4 weeks from the initiation of steel corrosion. In contrary, lower additions 26 were applied in the series CA II, and the same value of the $[Cl^-]/[NO2^-]$ ratio was approached after 11 weeks from the initiation of steel corrosion. They compared Impedance spectra (in Bode format) taken after these treatments. The capacitive response (a broad, asymmetrical peak of the phase angle) and large values of low frequency impedance for steel after the pre-passivation confirmed the development of passive film on steel surface. Dramatic change in impedance data was observed after subsequent exposure of pre-passivated steel in the chloride containing solution.

They found out that in early stages of the corrosion process calcium nitrite can be effective as a penetrating corrosion inhibitor when present in enough quantity and that the ability of calcium

nitrite to inhibit the initiated corrosion of steel depends not only on the chloride to nitrite ratio, but also on the time passing from the corrosion initiation. Also that the 27 polarization resistance or related parameters taken from impedance data can serve directly as an indicator of the corrosion behaviour of steel in concrete or concrete simulating solutions, without need of their conversion into corrosion current density.

Monticelli et al. (2000)

They studied the inhibiting behaviour of many organic and inorganic substances against steel corrosion in an alkaline chloride solution constituted by a saturated calcium hydroxide solution containing 0.1 M chloride ions. Besides 0.05 M sodium nitrite (SN), among the tested substances, only 0.005 M 5-hexyl-benzotriazole (C6BTA), 0.05 M sodium β-glycerophosphate (GPH), and saturated dicyclohexylammonium nitrite (DCHAMN) were able to prevent pitting corrosion over 30-day exposures to the aggressive electrolyte.

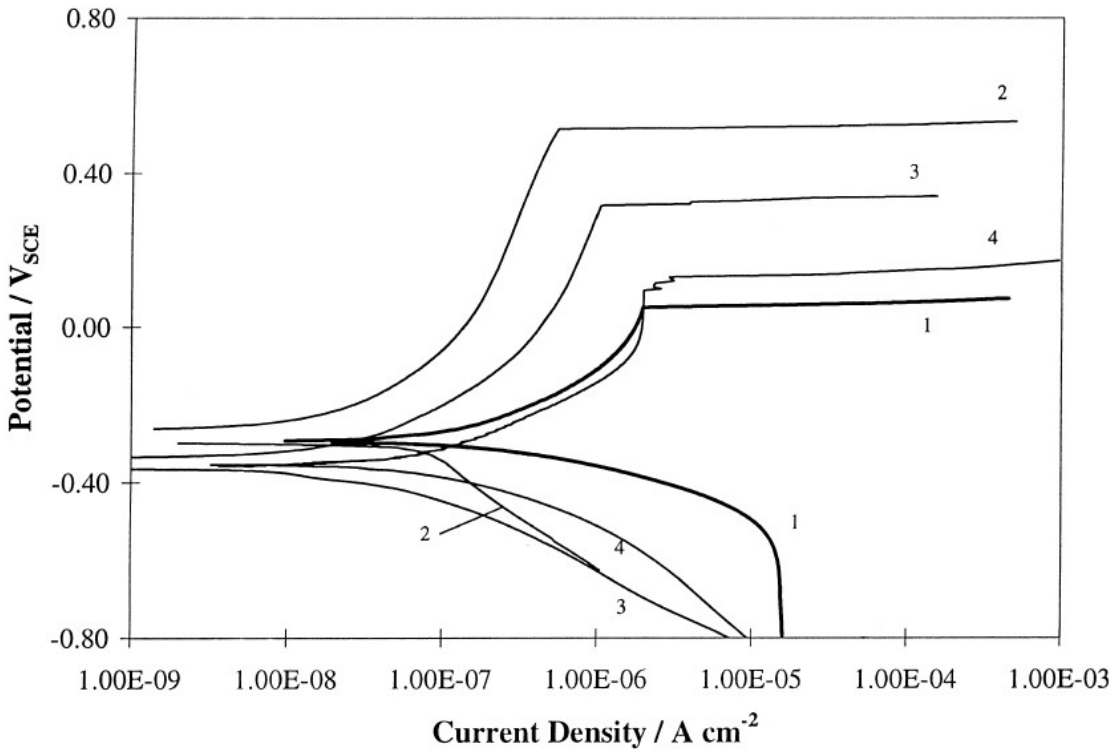


Figure 3.7 Polarization curves recorded in saturated $Ca(OH)_2$ solutions in the absence (1) or in the presence of the following additives: saturated DCHA (2), 0.005 M C6BTA (3), or saturated TSAH (4) ***(Monticelli et al. 2000)***

Moreover, very good results were obtained with steel specimens coated by DINITROL AV 30®, which is a commercial corrosion inhibitive filming product. Chloride polluted mortars embedding steel rods were also prepared to assess the influence of the most promising inhibitors, added either as admixtures or as impregnation agents, under conditions closer to those experienced in concrete. The inhibiting efficiencies (IE) were tested by Electrochemical Impedance Spectroscopy (EIS). Good results were obtained with admixed tungstosilicic acid (TSAH), with GPH or DCHAMN penetrated from the outside or in the presence of DINITROL AV 30® coating. Among the promising substances, only 0.05 M SN, 0.005 M C6BTA, 0.05 M GPH, and sat. DCHAMN are able to keep the inhibiting action throughout the exposure.

Trabanelli et al. (2005)

They made a synthetic solution (SS) by bubbling pure CO_2 in a saturated $Ca(OH)_2$ solution till obtaining pH 7 and then filtering it for electrochemical study on inhibitors of rebar corrosion in carbonated concrete. And concrete carbonation has been obtained by maintaining the concrete specimens in CO2 atmosphere for 80 days, at 68% RH and room temperature. In SS, benzoate, its aminoderivatives and dicarboxylates were able to form a long-lasting passive layer on the steel surface. Their efficiency improved with time. Then he find that after 1 h immersion, specimen omitting the very high frequency arc due to the low solution conductance, EIS spectrum of steel exhibited a single capacitive semicircle in the 103– 102 frequency range (Fig. 3.7), showing that the corrosion process was mainly charge-transfer controlled at short immersion times.

Among the additives tested as admixed inhibitors in carbonated concrete, only BEN (benzoic acid) and 2AMB (2-amino benzoic acid) exhibited some inhibitive effect towards the rebar corrosion process. However, in BEN-containing concrete specimen no inhibitive action was maintained till 400 days of exposure, while in the presence of 2AMB inhibiting efficiencies around 60% were still measured at the end of the test.

Figure 3.8 shows the experimental and simulated EIS spectra recorded in uninhibited SS at different immersion times.

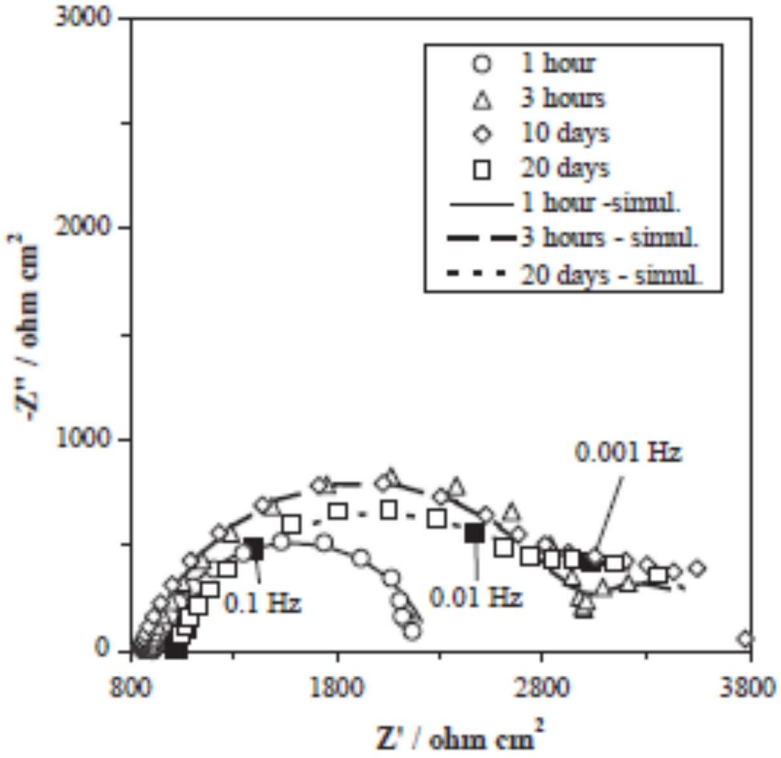


Figure 3.8 Experimental and simulated EIS spectra recorded in uninhibited SS at different immersion times *(Trabanelli et al. 2005)*

The inhibitor leakage is reputed responsible of the decrease with time in the inhibiting efficiency of both additives.

Monticelli et al. (2011)

In their paper they have studied about two corrosion inhibitors, that is sodium 2- amino-benzoate (2AMB) and sodium glycero-phosphate (GPH), in a synthetic solution simulating the composition of the pore solution in a carbonated concrete, containing chlorides. Tests have been performed to verify if the simultaneous use of the two substances is compatible and if their addition can efficiently hinder the corrosion attack in the presence of both chlorides and carbonation. The synthetic solution has been prepared by bubbling carbon dioxide through a saturated (and filtered) solution of $Ca(OH)_2$, containing 0.1M NaCl, in order to reach pH 7. He prepared ribbed AISI 1033 type steel bars of 10mm diameter, commercialized as concrete reinforcement (composition: C=0.31%; Mn=0.94%; Cr=0.26%; Ni=0.19%; Cu=0.50%; Si=0.14%; Co=0.02%; Al=0.04%; S=0.03%; balance iron) with exposed surface area of 4.5 cm^2. These electrodes are exposed to the

test solutions after grinding by emery papers up to grade 600, washing with double distilled water and degreasing with acetone.

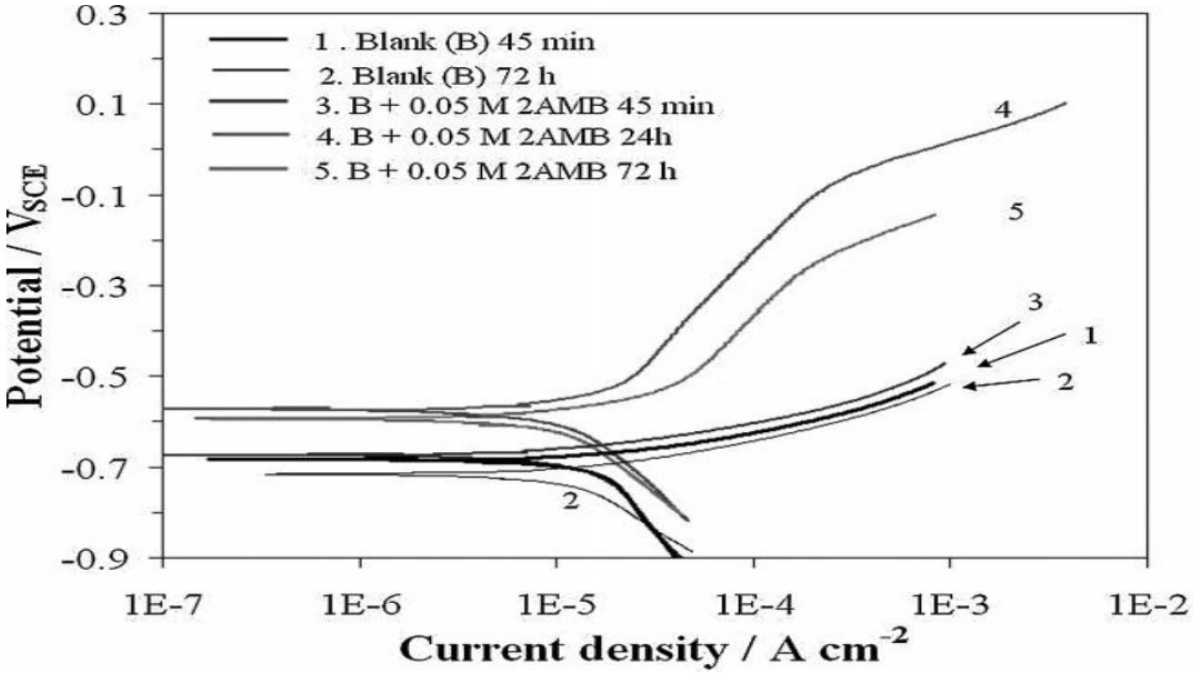


Figure 3.9. Polarization curves recorded on steel in carbonated chloride solution, both in the absence and in the presence of 0.05M 2AMB *(Monticelli et al. 2011)*

From this experiment he conclude that in carbonated chloride-containing solution (from here on the blank solution) no significant variation of steel corrosion behavior is achieved by prolonging the immersion period from 45 min up to 72 h. This suggests that the corrosion product film growing on the metal surface is not protective. At the end of the immersion period, Icorr. is close to 1.2 x 10^{-5} A/cm^2, as estimated by the Tafel method by extrapolation of the cathodic polarization curve.

The addition of 0.05M 2AMB to the blank solution affords no inhibiting effect on the corrosion process after 45 min. of immersion (Fig. 3.9). However, after 24 h of immersion Ecorr is ennabled up to -0.58 VSCE, owing to the increase in the slope of the anodic polarization curve, likely due to the formation of a surface film. The protectiveness of this film is scarce (as suggested by the measured Icorr values which are only slightly lower than those measured in the blank solution) and diminishes with time, as the anodic curve shifts again towards higher current densities, at the end of 72 h immersion (Figure 3.9).

Polarization curve recording and EIS technique have shown that the mixture inhibiting action develops slowly within 24 h, during which a surface porous film forms with a higher pore resistance and particularly a higher mass transport resistance with respect to those evaluated in the blank solution. The polarization curve analysis suggests that diffusion of Fe^{2+} cations from the metal surface to the aggressive solution may be the mass transport process controlling the steel corrosion rate in inhibited solutions.

M.O. Reilly et al. (2006)

Three commercially available corrosion inhibitors—calcium nitrite, a solution of amines and esters, and an alkenyl-substituted succinic acid salt—are evaluated in conjunction with conventional reinforcement in concrete based on corrosion rate, metal loss, the critical chloride corrosion threshold (CCCT) and pore solution analyses.

The first organic inhibitor in this study is a water-based organic corrosion inhibitor composed of amines and esters (AE). This inhibitor protects steel by adsorption of the amines on the surface of the reinforcement, where they form a protective film. In addition, this inhibitor forms an insoluble salt, blocking the pores in concrete and decreasing permeability. The second organic inhibitor (disodium tetrapropenyl succinate) is a salt of alkenyl-substituted succinic acid (ASSA). The polar end of the molecule binds to the steel, possibly stabilizing the passive layer. The molecule also exhibits hydrophobic properties, decreasing the tendency for moisture to enter concrete *(Wojakowski and Distlehorst 2009).*

The use of corrosion inhibitors extended the time to initiation, with average times to initiation of 19, 26, and 28 weeks for concrete containing AE, CN, and ASSA, respectively.

The average corrosion (metal) losses for the southern exposure specimens without and with corrosion inhibitors are shown in Fig. 3.10.

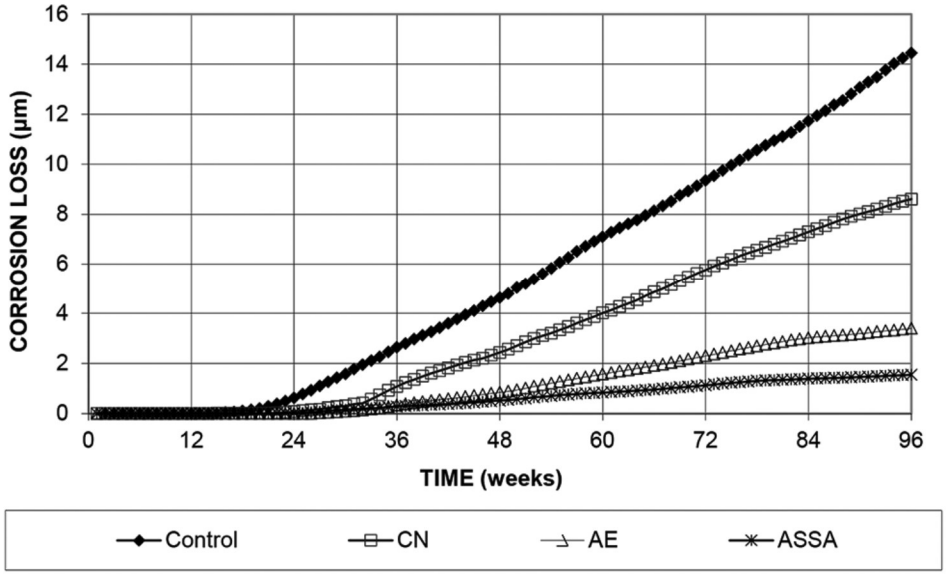


Figure 3.10 Average corrosion loss for southern exposure specimens without and with corrosion inhibitors. (Note: 1 mm = 0.0394 mils.) ***(M. O'Reilly et al. 2006)***

All three inhibitors tested in this study were effective in increasing the time to corrosion initiation and reducing the corrosion rate of reinforcing steel in concrete. Concrete containing ASSA was more effective at reducing corrosion rate overall.

Rankata et al. (2013)

They studied about the corrosion protection of steel with DMEA-based organic inhibitor. The test specimens considered for this study were cylinders 100 mm in height and 40 mm in diameter. One steel rebar was axially embedded in each cement mortar Cement, sand and water were mixed in a mortar mixer for approximately 5 min until a uniform consistency was achieved. The molds 100 mm in height and 40 mm in diameter were filled with mortar and vibrated for consolidation using a vibrating table. Copper wire cables were connected to the steel bar in order to receive electrochemical measurements.

Steel rebars were cleaned prior to their installation into the mortars according to ISO/DIS 8407.3 standards. In particular the surface of the steel bars was washed with water and then immersed in strong solution of HCl (500 ml HCl, density q = 1.19 g/ml in 1000 ml distilled water) with organic corrosion inhibitor (3.5 g hexamethylene tetramine in 1000 ml distilled water) for 15 min, washed with water and washed thoroughly with distilled water to eliminate traces of the corrosion inhibitor

and chloride ions. Following that, the surface was cleaned with alcohol and acetone and finally weighed to accuracy of 0.1 mg. Thereafter the 28 bars were placed in cylindrical moulds, where the mortar was cast and stored at ambient conditions in the laboratory for 24 h.

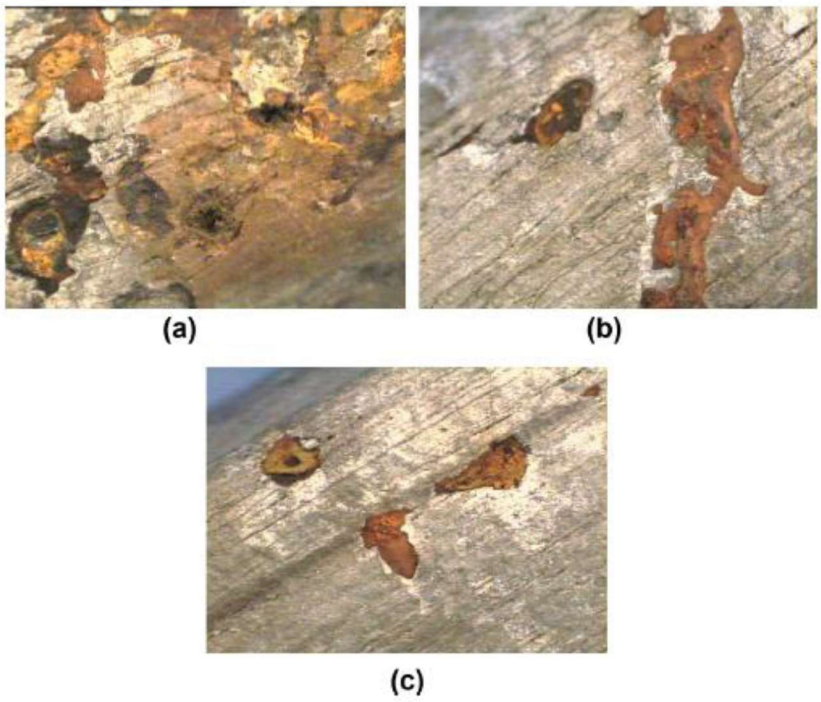


Figure 3.11 Fiber optical microscope images after 7 months partially immersion in 3.5 wt.% NaCl solution. Surface morphology of (a) steel reinforcement embedded in contaminated mortar with chloride ions (2 wt.% of cement), (b) steel reinforcement embedded in contaminated mortar with chloride ions (2 wt.% of cement) treated with corrosion inhibitor (DMEA 1 wt.% of cement) and (c) steel reinforcement embedded in contaminated mortar with chloride ions (2 wt.% of cement) treated with corrosion inhibitor (DMEA 2 wt.% of cement). For all the steel reinforcements the magnification used was 50 ***(Rankata et al., 2013)***

After being demolded the specimens were placed in water in curing room (RH > 98%, T = 20 ± 1.5 ºC) for 24 h and then kept for an additional 7 days at ambient temperature in a laboratory environment to stabilize internal humidity. Epoxy resin was placed in the region in order to avoid atmospheric corrosion. Finally the specimens were partially immersed in 3.5 wt.% NaCl solution up to 20 mm from the bottom. The objective of partially immersing 29 the cement mortar

specimens was to provide an increase of required moisture and oxygen for the initiation and acceleration of reinforcement corrosion. The chloride concentrations of the exposure solutions were selected to avoid leaching of chloride ions casted into cement mortar as contamination. The experimental duration of this study was 7 months.

Methods used to assess cement mortar specimens performance included the measurement of corrosion potential, corrosion rate and mass loss. The corrosion potentials for each of the test specimens were recorded at regular intervals versus a saturated calomel reference electrode (SCE). The measurements were initially recorded on an everyday basis until equilibrium conditions were established and then they were recorded on a weekly basis. Fibre optical microscopic images were also taken.

The corrosion potentials in cement mortar specimens contaminated with chloride ions shift to more negative values as the chloride concentration increases. On the other hand, when corrosion inhibitor is added, the corrosion potentials shift towards more positive values. The addition of 2 wt% of cement DMEA inhibitor decreases the mass loss of the steel rebar about 43%. The corrosion rate of steel reinforcement increases as chloride concentration increases. However, the corrosion rate of the rebars decreases as the concentration of the corrosion inhibitor increases. Figure 3.11 shows fiber optical microscopic images.

Hwa-Sung Ryu (2016)

They used commercially available N, N'-Dimethyl ethanol amine (DMEA) inhibitor and studied in different concentrations of NaCl in saturated $Ca(OH)_2$ solution. The performance of inhibitor was evaluated by potential time, electrochemical impedance spectroscopy and potentiodynamic techniques. This inhibitor was mixed in saturated $Ca(OH)_2$ solution and it was made in double distilled water by proper mixing. The pH of saturated $Ca(OH)_2$ solution was 12.60 at room temperature (25 ºC ± 1 ºC). Different concentrations of NaCl were mixed in saturated $Ca(OH)_2$ solution with different content of inhibitor. The mild steel rebars with 16 mm diameter were cut and mounted in acid/alkali resistance thermosetting resin. The mounted samples were polished with emery paper started from 180 to 1200 μ. Thereafter, cloth polished of steel rebar was carried out and degrease with acetone prior to start the electrochemical experiments.

Prior to start the experiments, steel rebars were exposed in solution and the potential was stabilized with potentiostat. These electrochemical studies were performed by three electrode systems where steel rebar work as working electrode (WE), platinum wire as a counter electrode (CE) and silver-silver chloride as a reference electrode (RE). The area of working electrode was 0.78 cm^2 and it was fixed for every samples.

The corrosion potential time studies were performed on steel rebars in saturated $Ca(OH)_2$ solution with different concentrations of NaCl and DMEA inhibitor. The corrosion potential time plots are shown in Fig 3.12.

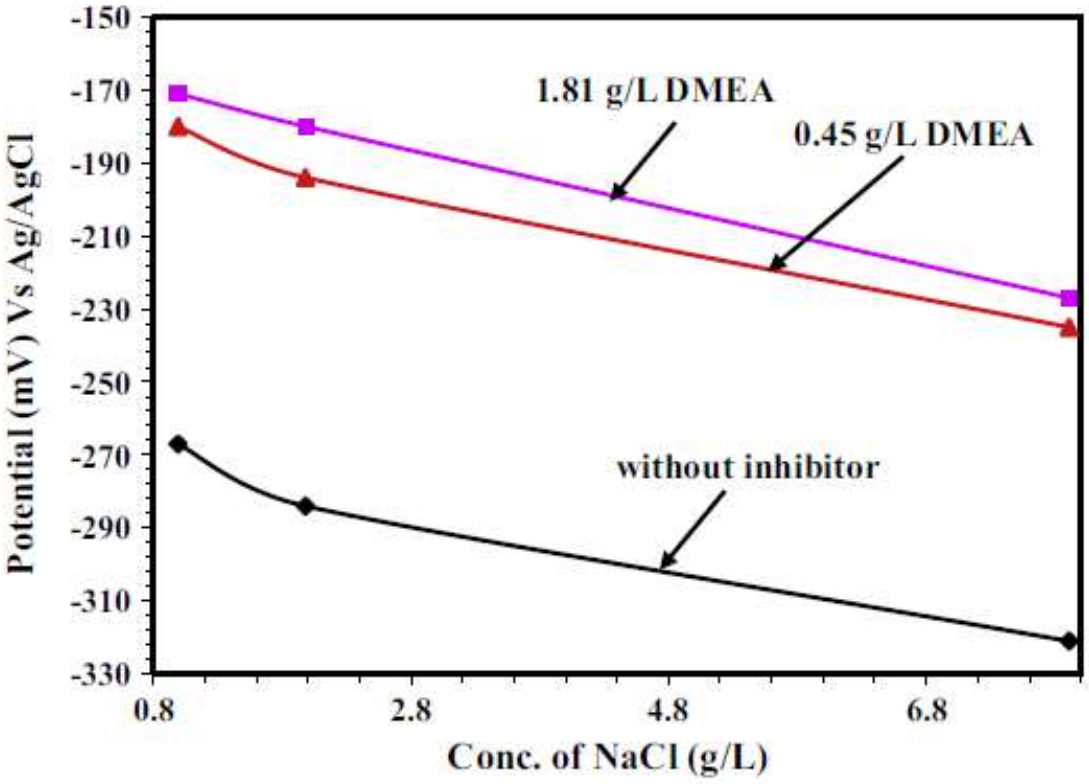


Figure 3.12 Corrosion potential-time plots of steel rebar exposed in saturated $Ca(OH)_2$ solution different concentrations of NaCl and DMEA inhibitor. ***(Hwa-Sung Ryu 2016)***

Yuming Tang et al. (2011)

They studied the inhibitive effects of several inhibitors for carbon steel in acidified pore solution (pH 8.0). Sodium tungstate and sodium molybdate are two kinds of environmental friendly inorganic inhibitors [8–13], which have been widely used for many applications, including engine coolants, paints and coatings, metalworking and hydraulic fluids, and cooling waters. However, these inhibitors are rarely used in acid polluted concrete environments. It is also reported that sodium phytate, an organic inhibitor, shows inhibitive effect for carbon steel in simulated pore solutions, and its strong chelate ability is available in a large pH range (14–8).

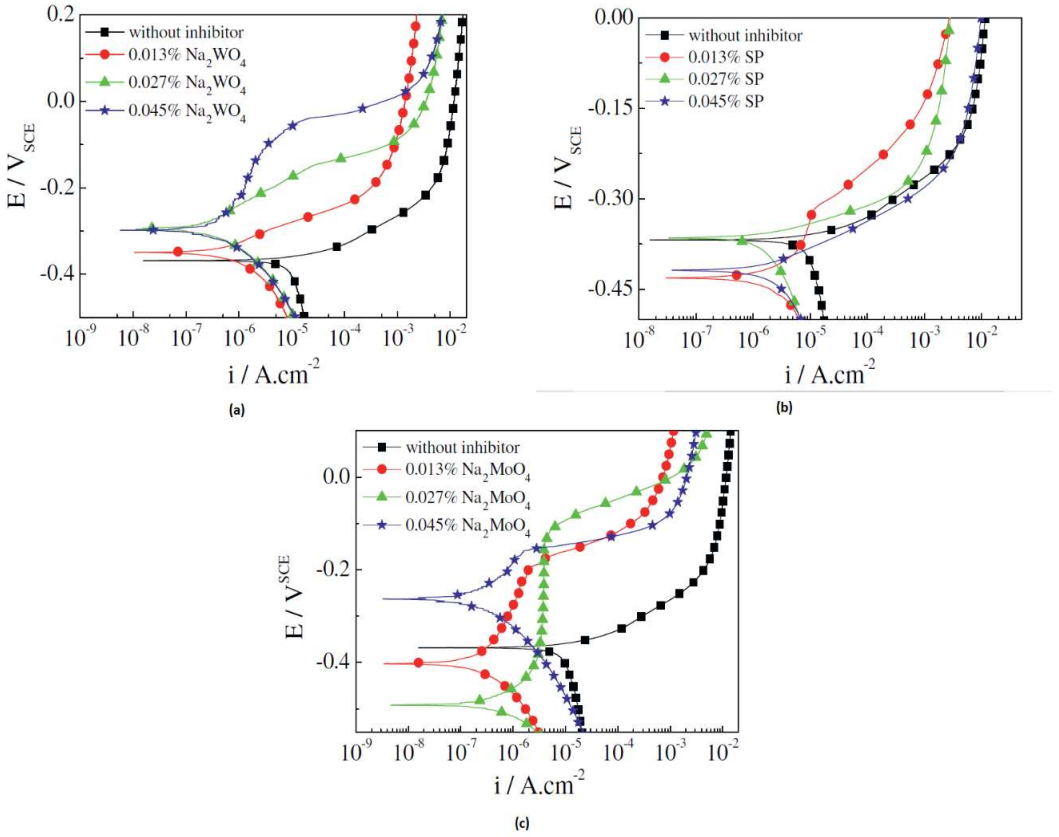


Figure 3.13 (a) Potentiodynamic polarization curves for steel samples in acidified pore solution (pH 8.0) containing Na_2WO_4 at low concentrations. (b) Potentiodynamic polarization curves for steel samples in acidified pore solution (pH 8.0) containing sodium phytate at low concentrations. (c) Potentiodynamic polarization curves for steel samples in acidified pore solution (pH 8.0) containing Na_2MoO_4 at low concentrations. *(Yuming Tang et al. 2011)*

They mainly studied the effects of sodium tungstate, sodium molybdate and sodium phytate as inhibitors at various concentrations in acidified saturated calcium hydroxide solution. Sodium nitrite and a commercial inhibitor named RSA were chosen as the reference inhibitors.

In ordinary pore solution (pH 12.5) the polarization curve of carbon steel shows an active–passive transition. Sodium molybdate, sodium tungstate and sodium nitrite at low concentrations (wt.% 6 0.045%) reveal effective inhibition effects by promoting passivation of the steel.

Molybdate and tungstate were present on the steel surface according to Raman spectrum analysis, which supports the adsorption mechanism of the inhibitors which results in the active polarization behavior of acidified pore solution (pH 8.0).

Sodium molybdate shows good effect to promote passivation at low concentrations (0.013 wt.%), but for sodium tungstate and sodium nitrite higher concentration (0.045 wt.%) is needed to obtain passivation. Sodium phytate only shows minor inhibitive effect at the concentration level of 0.045 wt.%. Whereas at higher concentration level (0.045% 6 wt.% 6 2%), the inhibitors sodium molybdate, sodium tungstate and sodium nitrite behaviour well in the acidified pore solution. When the concentration is above 0.5%, sodium phytate also shows inhibitive effect and passivation is promoted.

Hilke Verbruggen et al. (2016)

Their purpose of this research was to evaluate different inhibitors for both types of corrosion that can occur in reinforced concrete: pitting corrosion (by chloride attack), and uniform corrosion (by a drop in pH). Depending on where the inhibitors act a distinction can be made between anodic inhibitors, which impede the oxidation reaction, cathodic inhibitors, which decrease the reduction reaction, or mixed inhibitors which act on both half-reactions. Consequently, the inhibition effectiveness depends on the corrosive environment and the metal surface it needs to act on. The following inhibitors were used: Sodium molybdate dehydrate ($Na_2MoO^{4-}2H_2O$) with a purity P=99.0%; Cerium nitrate hexahydrate ($Ce(NO_3)^{3-}6H_2O$) with a purity = 99.0%; 2,5-Dimercapto-1,3,4-thiadiazole (DT) with a purity P98.0%; 2-Mercaptobenzothiazole (MBT) with a purity P97.0%; 1H-benzotriazole (BTA) with a purity P98.0%.

In this work they defined three critical situation that can realistically occur in reinforced concrete and thus in which an inhibitor should act. Those situations are: CPS 2%Cl^- , an alkaline concrete

pore solution of pH 13 with 2 wt% Cl^-, representing pitting corrosion; CPS carb, a carbonated solution of pH 9, simulating uniform corrosion; CPS carb+0:05%Cl^- , a carbonated solution of pH 9, also contaminated with 0.05 wt% Cl^-.

Often only one of these cases is considered, but regarding practical applications it is best to mimic realistic situations as good as possible. Thus it is important to consider both forms of corrosion, and even the combination of carbonation and presence of chlorides, when evaluating corrosion inhibitors for choosing the best possible candidate(s) to be used in reinforced concrete. For the case of pitting corrosion all the tested inorganic and organic inhibitors showed some inhibition, except for BTA. They can be ranked as follows, from least to best performing inhibitor:
DT and $Ce(NO_3)_3$ < Na_2MoO_4 < MBT.

Hwa-Sung Ryu (2017)

He studied the effect of $LiNO_2$ and it was evaluated by electrochemical impedance spectroscopy (EIS) and potentiodynamic studies. $LiNO_2$ works as mixed type corrosion inhibitor by stabilizing the iron oxides/hydroxides in their stable form and stifle the corrosion of steel rebar. Different concentrations of dissolved $LiNO_2$ inhibitor solution was added in saturated $Ca(OH)_2$ with different content of NaCl. The solution was made in double distilled water by mixing them vigorously. The pH of this solution was 12.5 (±0.1) at 25 ºC (±1 ºC). In this study different molar ratio of [Cl^- /NO_{2-}] i.e. 0 (without inhibitor), 0.3 and 0.6 were taken to study the effect of $LiNO_2$ inhibitor with 0.99, 3.96 and 7.91 g/L NaCl.

The black milled scale of 16 mm steel rebar was descaled by using 10 v/v% of HCl, ringed with distilled water and dried. After descaling of milled scale from steel rebar surface, it was cut and mounted in acid/alkali resistance thermosetting resin. The mounted steel rebar was abraded with emery paper started from 180 to 1200 µm. Thereafter, cloth polished of steel rebar was carried out and degreased with acetone prior to start the electrochemical experiments.

Prior to start the experiments, the steel rebars were exposed in inhibitor and without inhibitor containing saturated $Ca(OH)_2$ solutions to stabilize the potential with potentiostat. Electrochemical studies were performed by three electrode systems where steel rebar work as working electrode (WE), platinum wire as a counter electrode (CE) and silver-silver chloride as a reference electrode (RE).

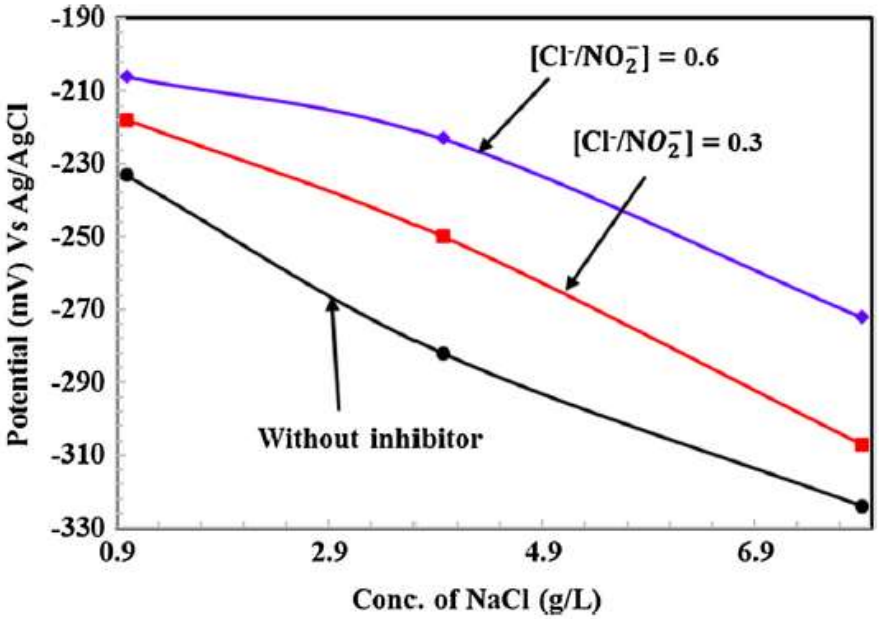


Figure 3.14 Corrosion potential plots of steel rebar exposed in saturated $Ca(OH)_2$ solution with different concentration of NaCl at different molar ratio of [Cl^- /NO_2^-] *(Hwa-Sung Ryu 2017)*

The WE and RE were fixed in such a manner that both are close to each other, since there will be less solution resistance caused. The area of working electrode was 0.78 cm^2 and it was fixed for every sample.

The corrosion potential of steel rebars were measured in saturated $Ca(OH)_2$ with different content of NaCl at different molar ratio of [Cl^- /NO_2^-] and it is shown in Fig 3.14.

3.3 SUMMARY

In last two decades, corrosion inhibitors have been extensively used to protect steel reinforcement in RC structures. There are plenty of corrosion inhibitors available commercially. Most of the commercially available corrosion inhibitors are used for chloride (Cl-) induced corrosion and are not effective for carbonation induced corrosion.

Commercially available corrosion inhibitors being very expensive affect the total cost of structure. Growing need of corrosion inhibitors is expected in future because of environment becoming aggressive due to increasing pollution. Due to which, there arises a need to find a cheaper replacement of these corrosion inhibitors.

In this research work, attempts have been made to find some cheaper chemicals which can replace the expensive commercial corrosion inhibitors. Effectiveness in corrosion inhibition of some commonly available cheap organic chemicals is evaluated in the present study.

CHAPTER 4 EXPERIMENTAL PROGRAM

4.1 GENERAL

In this chapter, the experimental setup is presented to find out the effect of various corrosion inhibitors in mitigating carbonation and chloride induced corrosion in steel. The different types of tests which are used in monitoring progression of corrosion on steel are HCP and LPR sweep test. Experimental setup and details of following electrochemical tests is discussed in the following sections.

4.2 MATERIALS USED:

For conducting the experiments, the materials used are High Yield Strength Deformed Steel bars, chemical corrosion inhibitors and epoxy. Details of the following materials are described as under.

4.2.1 Steel Reinforcement

HYSD steel bars of 60mm in length and 12mm in diameter are used for conducting experiments. The various physical and chemical properties of HYSD Fe500 steel bars used, are given in the Table 4.1.

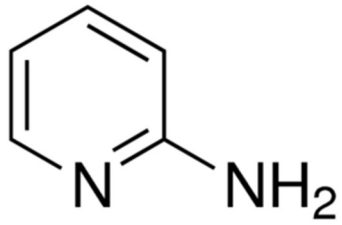
Table 4.1 Physical and Chemical composition of steel bars used for experimental work *(www.tatatiscon.co.in)*

Properties	Constituent	Fe500 (% Max.)
Chemical properties	Carbon	0.30
	Sulphur	0.055
	Phosphorous	0.055
	Nitrogen (PPM)	120
Physical properties	Minimum Yeild Stress (N/mm^2)	500 N/mm^2
	Minimum Ultimate Tensile Strength (N/mm^2)	601 N/mm^2
	Minimum Elongation %	12.0

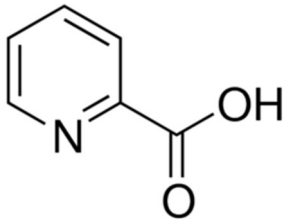
4.2.2 Corrosion Inhibitors

Corrosion inhibitor is principally a chemical compound, which when added to a liquid or a gas, decreases the rate of corrosion. In this study, various types of chemical corrosion inhibitors were used to increase the corrosion resistance of HYSD steel bars. The chemicals were selected upon their power of interrupting the corrosion process and their potential to be used as corrosion inhibitor. Various corrosion inhibitors that were used for the experiment purpose are listed in Table 4.2.

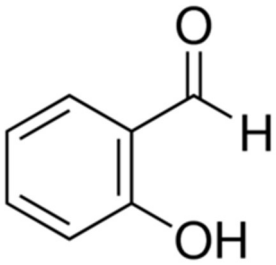
Molecular structures and names of the chemical compounds are shown in Fig. 4.1.



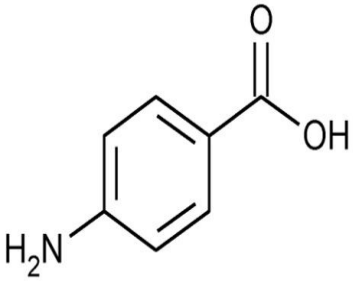
2-Aminopyridine



2-Picolinic Acid



Salicylaldehyde



4-Aminobenzoic Acid

Figure 4.1 Molecular structures of compounds used as corrosion inhibitors

Table 4.2 Chemical corrosion inhibitors used for experimental work

Chemical	Chemical Formula	Molar Mass (gm/mol.)	Appearance	Density (g/cm^3)	Abbreviation used
2-Aminopyridine	$C_5H_6N_2$	94.12	Colorless solid	1.21	APD
2-Picolinic Acid	$C_6H_5NO_2$	123.11	White Solid	1.025	PA
Salicylaldehyde	$C_7H_6O_2$	122.12	Dark Green Oil	1.146	SCD
4-Aminobenzoic Acid	$C_7H_7NO_2$	137.14	White Powder	1.374	ABA

4.2.3 Chemical Compounds required to make pore solution

To simulate the environment of concrete, pure $Ca(OH)_2$ was used. Distilled water was taken to make all solutions in order to eliminate presence of any hardness in water.

To attain an environment which simulated a concrete specimen under the influence of carbonation and chloride induced corrosion, pure NaCl and Carbon Dioxide gas from a standard CO_2 cylinder of 99% purity for the purpose of bubbling were respectively used. Properties of these compounds are shown in Table 4.3.

Table 4.3 Properties of chemical compounds

Sr. No.	Compound	Molecular Formula	Molar Mass	Appearance	Odour	Density	Melting Point
1.	Calcium hydroxide	$Ca(OH)_2$	74.093	White powder	Odourless	$2.211 g/cm^3$	580 °C
2.	Sodium Chloride	NaCl	58.44	White powder	Odourless	$2.165 g/cm^3$	801 °C

4.2.4 Epoxy

Fevitite rapid is a two component multipurpose epoxy adhesive. It contains resin and hardener which are mixed in the ratio of 1:1, these two compounds are mixed few seconds before it is to be used. In these experiments, it was used to prevent some part of steel bar from chemically reacting with the pore solution.

4.3 PREPARATION OF SPECIMENS

Steel bars of 12mm diameter were cut into required lengths of 60mm each. Each of these were drilled and threaded at one end according to the necessity of the electro-chemical cell and the various tests. The diameter of drill was kept as 4mm and the depth was kept as 10mm so that proper conductivity of electricity can be ensured.

Each piece of steel bar of length 60mm was rubbed by wire brush and sand paper to remove any rust present on the surface. They were then further cleaned by soaking in analytical reagent grade hexane and allowed to air dry. After air drying the specimens for 24 hours, they were coated with one layer of epoxy which is followed by another layer of epoxy having a time difference of minimum one hour between these two layers. The resulting specimens after epoxy coating were kept for 24 hours. After that a nut with two bolts on it were screwed into the hole that was prepared and a copper wire is tightened between the bolts so as to ensure proper electrical conductivity.

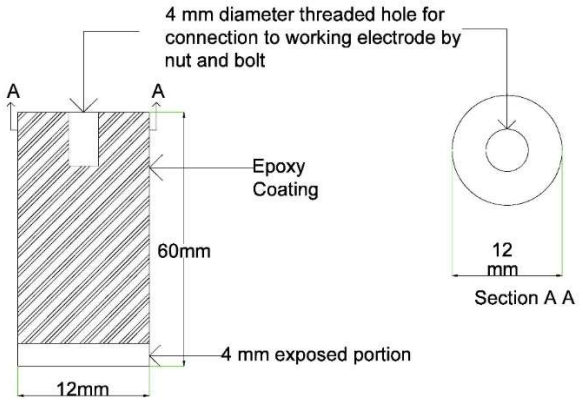


Figure 4.2 Cross-sectional details of prepared steel specimen used for experimental works

Figure 4.2 shows the line diagram of final steel specimen and Figure 4.3 shows the final prepared steel bars, which were ready for further experimentation after coating.

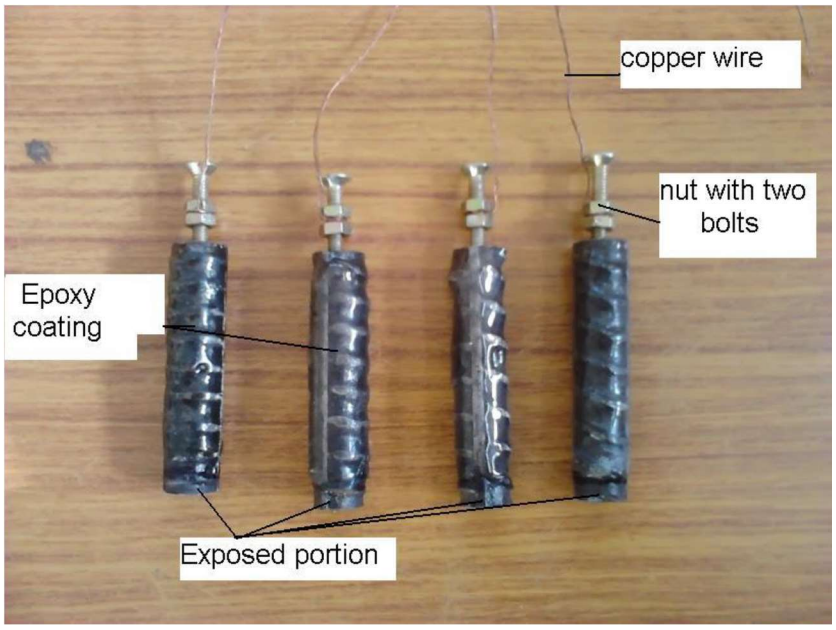


Figure 4.3 Cross-sectional details of prepared steel specimen used for experimental works

4.4 PREPARATION OF SYNTHETIC PORE SOLUTIONS

The preparation of pore solutions which were simulating freshly prepared concrete and concrete under carbonation and chloride attack respectively are discussed in the following parts.

4.4.1 Pore solution simulating freshly prepared concrete

To obtain a pore solution whose pH ranges from 12-13, simulating freshly prepared concrete, saturated solution of $Ca(OH)_2$ was prepared. Calcium hydroxide solution is also known as lime water. A fully saturated solution was prepared by taking 2.7gm/liter (0.035M solution) of calcium hydroxide in de-ionized or distilled water (to ensure there will not be any foreign mineral or chemical that are present in tap water, which can affect the resultant pH of solution). This solution was then mixed properly and left for at least 24 hours in a sealed container so that it didn't absorb any CO_2 from the atmosphere. After 24 hours, the resultant solution was filtered through a filter paper in a sealed container. The exposure of solution to the atmosphere was kept to be minimum so as to get optimum results.

After filtering, the pH of pore solution was checked and was found to be 12.6.

4.4.2 Pore solution simulating concrete under carbonation and chloride attack

To make a synthetic solution simulating concrete which is under carbonation and chloride attack, the pH value of the saturated calcium hydroxide solution was decreased from 12.6 to around a value of 7.4 by carbonating the saturated $Ca(OH)_2$ solution (passing CO_2 gas), and by adding pure NaCl in resultant solution.

To prepare the carbonated solution, Standard CO_2 of 99% purity was simply bubbled through the pore solution. Bubbling of CO_2 gas was done to achieve the carbonation condition in pore solution. Purpose of this process was to simulate corrosion prone carbonation state in the pore solution. The pH value of solution was reduced from 12.6 to 7.4 due to carbonation of calcium hydroxide. By reducing the pH value of solution to 7.4, a state of extreme carbonation in pore solution was achieved. CO_2 reacts with calcium hydroxide present in lime water to produce calcium carbonate ($CaCO_3$) precipitates. This process was monitored properly as the process converting calcium hydroxide into calcium carbonate while CO_2 bubbling is very fast, an eye should be kept on the pH throughout the process.

Pure Sodium Chloride (NaCl) was added into the resultant solution, at a quantity of 3.5% w/w. The resultant solution then was filtered by filter paper in order to remove any kind of suspension present in solution.

This solution was taken as the reference solution in order to study the effectiveness of different corrosion inhibitors, by using direct current DC corrosion measurement techniques.

This reference solution simulates a concrete specimen, in which the chlorides and the CO_2 are breaking the passive layer around steel surface and hence accelerating the corrosion process, results in rapid corrosion of steel bar. However in order to slow down this process various solutions are made by adding different corrosion inhibitors, where the inhibitor will resist the corrosion process by forming a passive layer around steel bar.

Details of the various synthetic pore solutions along with their corresponding nomenclature used are provided in the Table 4.4.

Table 4.4 Details of solutions used for experiments

Sr. No.	Abbreviations	Details of Solution
1.	Sol. 1	Saturated Calcium hydroxide solution (pH=12.6)
2.	Sol. 2	Sol. 1 + CO_2 + NaCl (pH=7.4)
3.	Sol. 3	Sol. 2 + Picolinic Acid Solution (1%w/w)
4.	Sol. 4	Sol. 2 + 2-Aminopyridine solution (1% w/w)
5.	Sol. 5	Sol. 2 + 2-Salicylaldehyde solution (1% w/w)
6.	Sol. 6	Sol. 2 + 4-Aminobenzoic Acid solution (1% w/w)

4.5 TESTING PROCEDURE

Different steel bars were used for every pore solution. These steel bars were coated with one layer of epoxy along the length leaving a length of 4mm from the bottom as discussed in the previous sections. After an hour when the first layer of epoxy had completely dried, another layer of epoxy was applied again, so as to ensure that epoxy layer didn't breaks during the experiment. The bottom uncoated length of the six different steel bars were submerged in four different chemical corrosion inhibitors solution to understand their effectiveness to prevent corrosion. Along with this, two test specimens were submerged partially in control solutions Sol. 1 and Sol. 2, one of calcium hydroxide and other of carbonated solution along with chlorides respectively, to compare the results with un-carbonated and carbonated stages respectively.

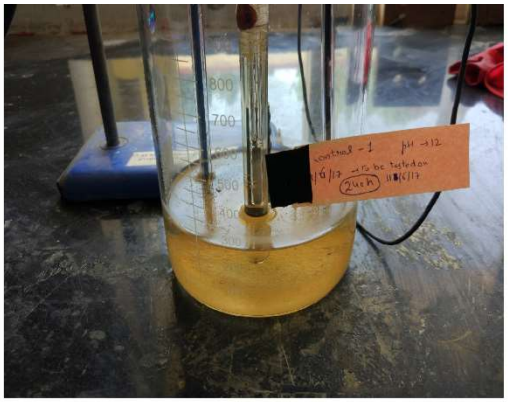
Final synthetic pore solution with different chemical corrosion inhibitors are shown in Figure 4.4.

Figure 4.4 Final Solutions of Chemical Inhibitors in Carbonated Saturated NaCl.

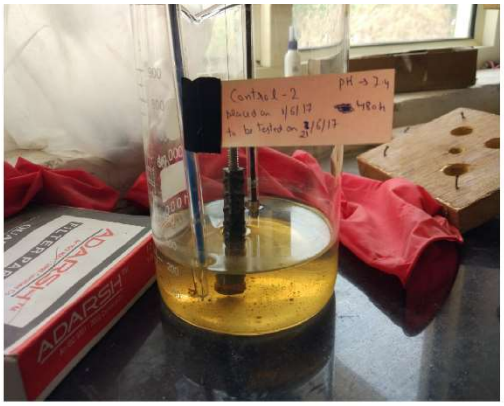
The steel bar specimens were monitored for 6 different periods of time i.e. 1hour, 24 hour, 48 hours, 120 hours, 240 hours, 480 hours respectively. 480 hours was the maximum time for which a specimen was being monitored. It is to be mentioned here that, in all these tests same reference electrode was used. Due to this the, solution was disturbed whenever the reading was taken. In order to avoid any error due to this, the system was kept untouched for 45 minutes prior LPR and OPC readings.

A total of 6 steel specimens were tested for each solution for 6 time intervals respectively, resulting in a total of 36 steel specimens. For testing a steel bar, every time a new solution was prepared, as due to the residuals of the respective steel specimen the solution was not appropriate for any further testing.

Figure 4.5 shows final prepared specimen for testing steel bars.



(a)



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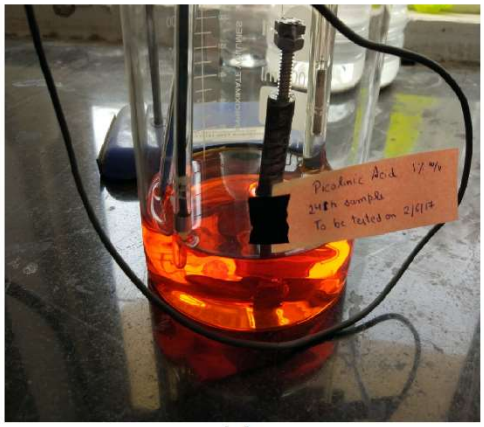
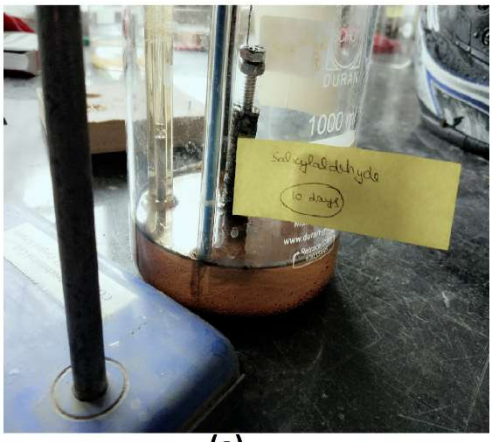
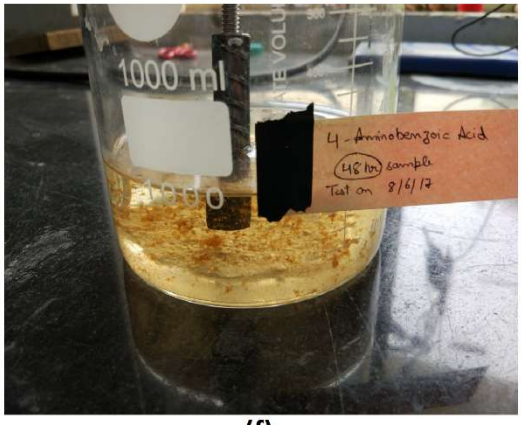


(c)

(d)



(e)



(f)

Figure 4.5 Final prepared specimens.

(a) Solution 1 (b)Solution 2 (c)Solution 3 (d)Solution 4 (e)Solution 5 (f) Solution 6

4.6 CORROSION MONITORING

After preparing the solutions with chemicals that were being used to check their efficiencies as corrosion inhibitors, steel specimens were placed in them after the epoxy has dried properly and then monitored. Two electrochemical tests were conducted to monitor corrosion activity i.e. Half-Cell potential measurement and corrosion current density measurement. Corrosion monitoring was done in 6 intervals; 1 hour, 24 hours, 48 hours, 120 hours 240 hours and 480 hours. Corrosion monitoring was done by using ACM field machine. Figure 4.6 shows the set up for long term LPR and HCP test.

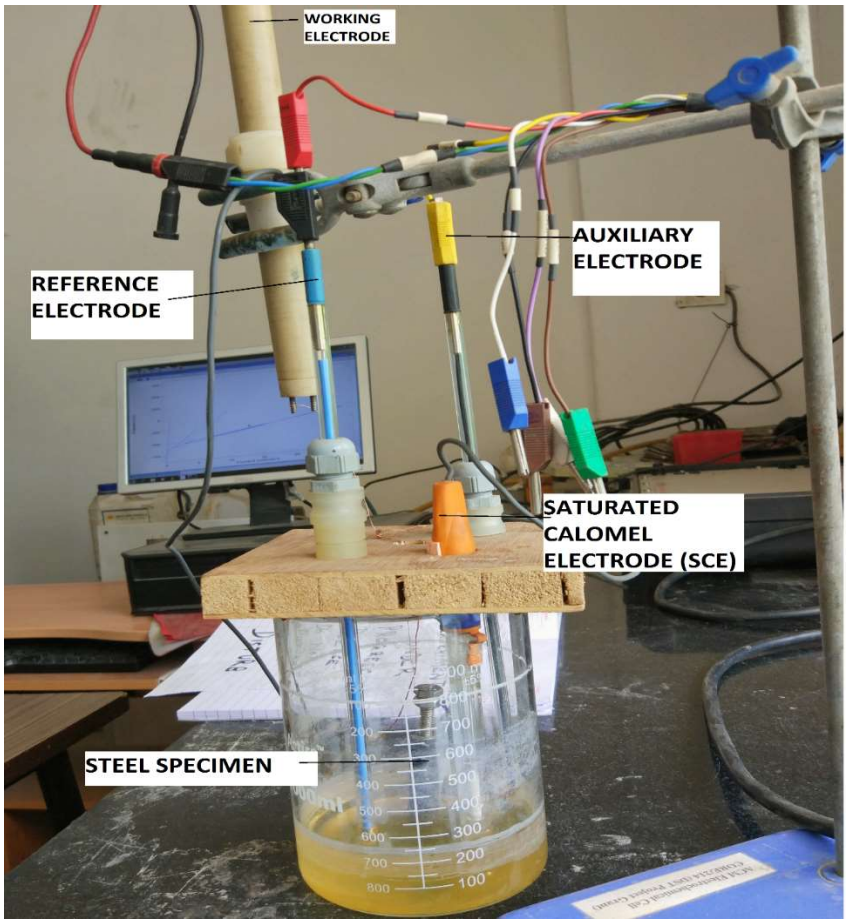


Figure 4.6 Setup for LPR and HCP tests

4.6.1 Equipment Used

ACM Model: Serial No. 1463 Field Machine, was used for corrosion monitoring. ACM field machine provides many electrochemical techniques like current & voltage / time, long term- LPR

sweep, long term- LPR step, Galvanostatic, AC impedance and Potentiostatic for corrosion monitoring.

Current & voltage / time, long term- LPR sweep techniques were used for this experiment. ACM field machine used for the experiment is shown in figure 4.7.

Figure 4.7 ACM Model: Serial No. 1463 Field Machine

4.6.2 Current and Voltage per time

In this experiment, all the specimens were monitored time to time by half-cell potential using a saturated calomel reference electrode (SCE) which consists of KCl (Potassium Chloride) by placing the electrode in the solutions. The procedure opted was followed by ASTM Standard **(**ASTM C 876 – 91). The half-cell potential measurement is the most common method used in corrosion surveys. An indication of the relative probability of corrosion activity can be obtained, by comparing the half-potential readings obtained by the test results and the half-cell potential readings standardized. The ASTM interpretation of half-cell potential (SCE) is summarized in Table 4.7.

Table 4.5 ASTM Interpretation of Half-Cell Potential Readings

Half-Cell Potential values	Corrosion condition
< -426 mV	Severe corrosion, corrosion induced cracking may occur
< -276 mV	High risk, 90% probability of corrosion
-126 to -275 mV	Intermediate risk, corrosion activity in reduction
0 to -125 mV	Low risk, 10% probability of corrosion

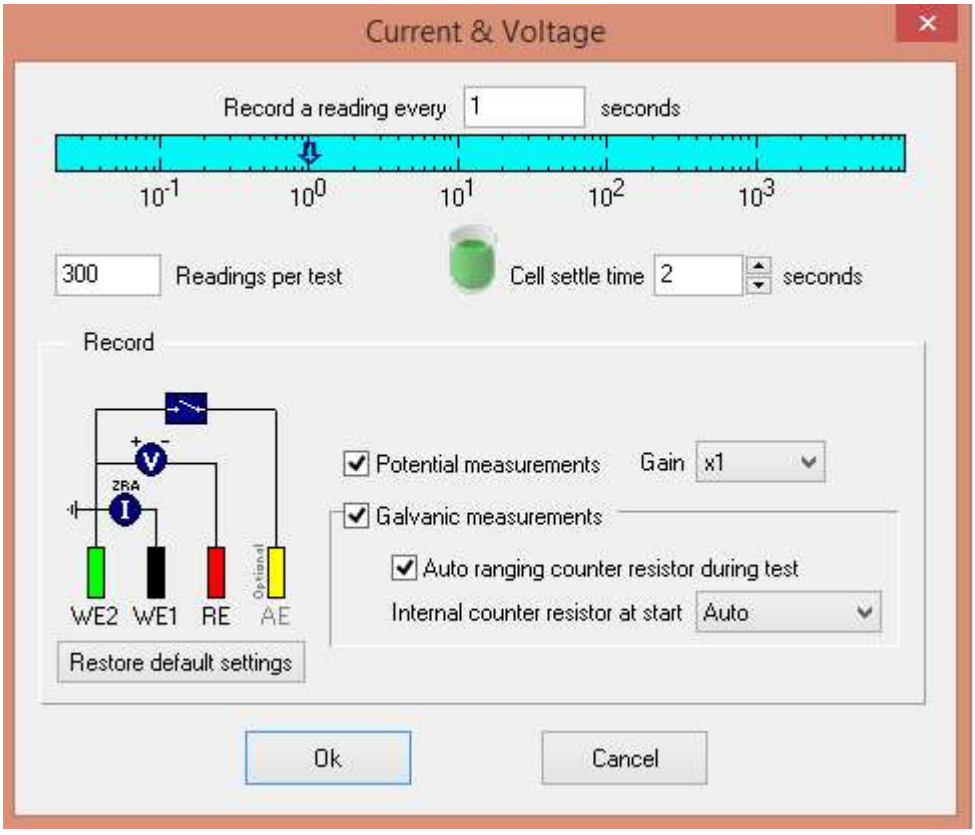


Figure 4.8 Input for current and voltage per time

4.6.3 Long Term- Linear Polarization Resistance Sweep

Long term LPR sweep or potentiodynamic polarization was done to find corrosion current density. The LPR technique has become a well-established method of determining the instantaneous corrosion rate measurement of reinforcing steel in concrete. The technique is rapid and non-intrusive, requiring only localized damage to enable an electrical connection to be made to the reinforcing steel. Due to the widespread corrosion of reinforcing steel in concrete structures there has been a huge demand for the development of non-destructive techniques to enable accurate assessment of the condition of reinforced concrete structures. LPR monitoring has been developed to fulfill this need.

The technique is rapid and nonintrusive, requiring only a connection to the reinforcing steel. The data provides a valuable insight into the instantaneous corrosion rate of the steel reinforcement, giving more detailed information than a simple potential survey. The LPR data enables a more detailed assessment of the structural condition and is a major tool in deciding upon the optimum remedial strategy to be adopted. It is thus vital that the LPR measurements obtained are accurate. In LPR measurements the reinforcing steel is disturbed by a small amount from its equilibrium potential. This can be accomplished potentiostatically by changing the potential of the reinforcing steel by a fixed amount, ΔE, and monitoring the current decay, ΔI, after a fixed time. Alternatively it can be done galvanostatically by applying a small fixed current, ΔI, to the reinforcing steel and monitoring the potential change, ΔE, after a fixed time period. In each case the conditions are selected such that the change in potential, ΔE, falls within the linear Stern–Geary range of 10 – 30 mV.

The polarization resistance, Rp of the steel is then calculated from equation

$Rp = \Delta E/\Delta I$

From which the corrosion rate, Icorr can be then calculated

$Icorr = B/Rp$

Where B is the Stern-Geary constant and is given by $B = \frac{(\beta a \times \beta c)}{2.3\,(\beta a + \beta c)}$

β_a and β_c are anodic and cathodic tafel constants respectively. The value of B is taken as 26mV considering steel in active condition. Rp is the polarization resistance.

A value of 26 mV has been adopted for active steel and 50 mV for passive steel. In order to determine the corrosion current density (Icorr) the surface area (A) of steel that has been polarized needs to be accurately known: Icorr = Icorr/A.

In this experiment potentiostatic linear sweep test was carried out on bare steel specimens using the ACM Field Machine. The electrochemical cell consists of a beaker with a wooden lid. It is provided with fittings for connecting the auxiliary electrode, reference electrode, and the specimen. Throughout the test, the reference electrode used was saturated calomel electrode (SCE). For testing, the bare steel specimen screwed to the working electrode, the reference electrode and auxiliary electrode were attached to the electrochemical cell. The potentiostatic linear sweep test was carried out from -250 mV to 1500 mV with offset from corrosion potential at a sweep rate of 60 mV per minute. The input readings of ACM field machine while performing this test are shown in Figure 4.9.

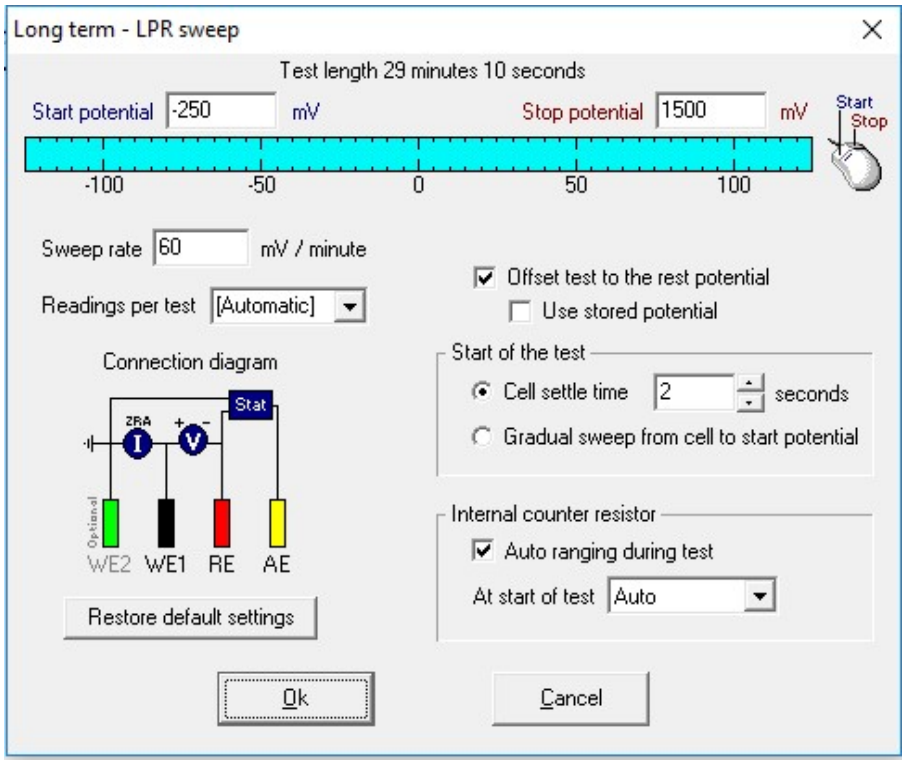


Figure 4.9 Input screen for long term LPR

5.1 GENERAL

This chapter presents the experimental results with a discussion of their significance. As was discussed earlier, the main objective of this research was to study the corrosion resistance provided by the various corrosion inhibitors in pore solutions simulating the environment of freshly prepared concrete and of concrete under carbonation and chloride ion attack. The tests were performed using direct current DC corrosion measurement techniques. The following sections discuss the results based on the data from Half-Cell potential and Linear Polarization Resistance sweep tests.

5.2 EXPERIMENTAL DETAILS

For conducting experiments, 1% solutions w/w of all chemical compounds were used. Details of the specimens are provided in the Table 5.1.

Steel specimens were immersed partially in these solutions up to a maximum period of 480 hours. Monitoring of corrosion was done at 1 hour, 24 hours, 48 hours, 120 hours, 240 hours and 480 hours of immersion. Current and voltage per time and Long term LPR with Tafel extrapolation techniques were used for monitoring of corrosion.

Table 5.1 Details of solutions used for experiments

Sr. No.	Abbreviations	Details of Solution
1.	Sol. 1	Saturated Calcium hydroxide solution (pH=12.6)
2.	Sol. 2	Sol. 1 + CO_2 + NaCl (pH=7.4)
3.	Sol. 3	Sol. 2 + Picolinic Acid Solution (1%w/w)
4.	Sol. 4	Sol. 2 + 2-Aminopyridine solution (1% w/w)
5.	Sol. 5	Sol. 2 + 2-Salicylaldehyde solution (1% w/w)
6.	Sol. 6	Sol. 2 + 4-Aminobenzoic Acid solution (1% w/w)

The brief details of tests performed are described in the following sections.

5.2.1 Half-Cell potential Measurements

Half-cell potentials (also referred as the equilibrium potential, the rest potential (Rp), or the corrosion potential) was measured on the reinforcing steel bars. Half-cell potential readings were taken with respect to Saturated Calomel electrode (SCE) as reference electrode. The value of half-cell potential obtained gives an indication of de-passivation of steel and hence the possibility of corrosion. ASTM C876- 91 suggests that the possibility of rebar corrosion, embedded in concrete when the Half-cell potential is lower than -276 mV (SCE) is higher than 90%. In addition, when the Half-cell potential is more than -126 mV (SCE) the corrosion risk is lesser than 10%. However between these values of -126mV and -275mV, the probability of corrosion is intermediate. Table 5.2 presents ASTM Interpretation of Half-Cell potential readings provided in ASTM C 876 – 91.

Table 5.2 ASTM Interpretation of Half-Cell Potential Readings

Half-Cell potential values	**Corrosion condition**
< -426 mV	Severe corrosion, corrosion induced cracking may occur
< -276 mV	High risk, 90% probability of corrosion
-126 to -275 mV	Intermediate risk, corrosion activity in reduction
0 to -125 mV	Low risk, 10% probability of corrosion

5.2.2 Linear Polarization Resistance (LPR)

Linear Polarization Resistance sweep monitoring for measuring corrosion is an effective electrochemical method. Observing the relationship between electrochemical potential and current generated between electrically charged electrodes in a process stream that allows the calculation of the corrosion rate. As compared to other electrochemical techniques for measuring corrosion resistance, the LPR effectiveness in pore solutions is maximum, and has confirmed to be a technique of rapid response. *(www.acminstruments.com/techniques)*

The linear sweep test was conducted on bare steel specimen. Anodic polarization curve were obtained for different types of corrosion inhibitors. A typical LPR graph shows different zones of corrosion for the steel reinforcement, which are indicated as follows:

Active zone

It is the zone where, when a very little change in potential is promoted, the increase in current density is significantly high.

Passive zone

The zone where the change in current density is relatively small with significant increase in potential is promoted, it lies above the active zone.

Pitting zone

The pitting zone is a zone with oxygen evolution, which results in pitting corrosion, lies above the passive zone.

These 3 different zones for control Sol.1 are shown in a typical anodic polarization curve in Figure 5.1.

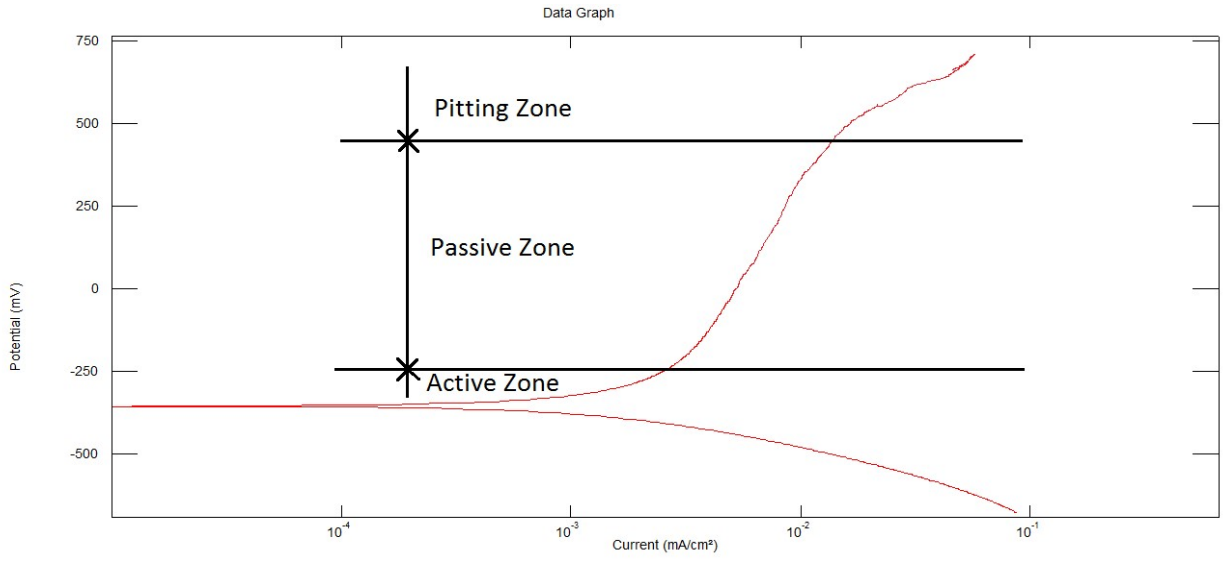


Figure 5.1 Anodic polarization curve for Sol. 1.

A solution with a pH of 8 causes a significant increase in anodic current density associated with a marked loss of passivity. As a result, the passive region is replaced by a range of potentials characterized by strong active dissolution. Thus, as the pH drops, the passivation region disappears

and the steel undergoes severe active dissolution. *(Tommaselli et al.2009).* The curve then doesn't show any specific passive zone.

When the rebar loses its passivity the anodic polarisation curve does not show any distinction between different zones. These comparison between two typical curves are shown in Figure 5.2.

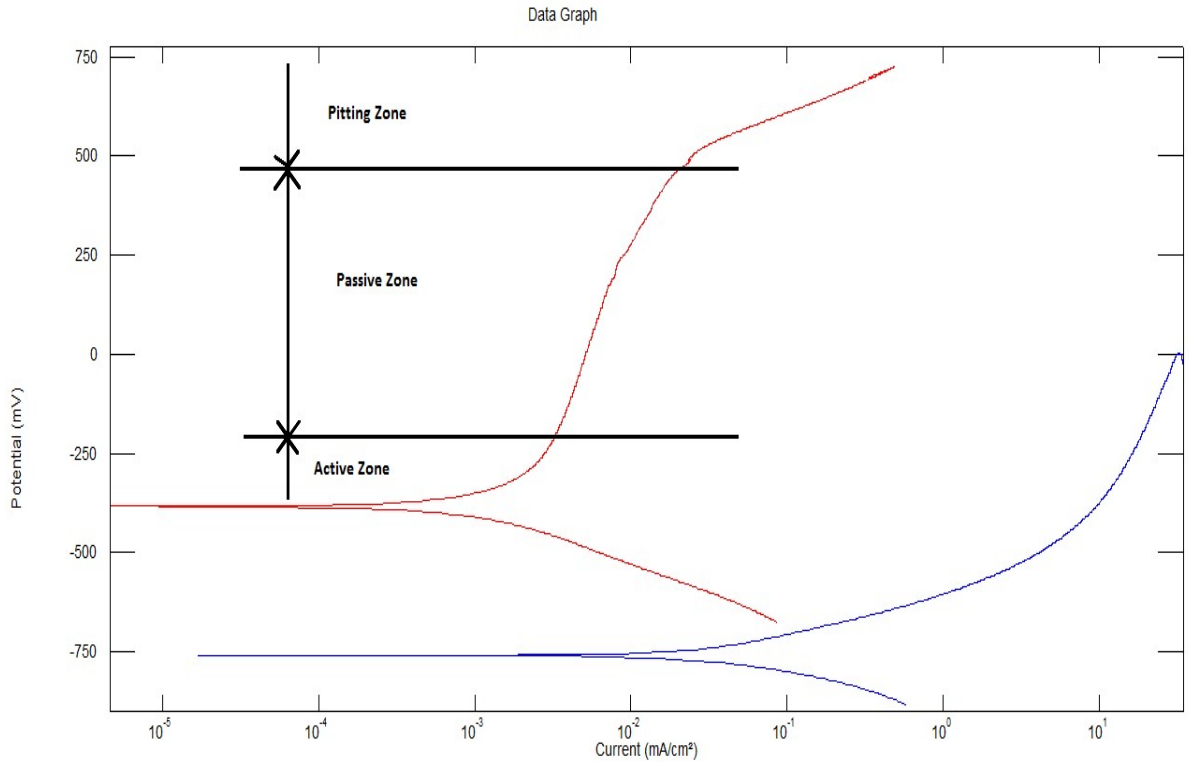


Figure 5.2 Anodic polarization curve for Solution 1 vs Solution 2

Figure 5.2 shows the anodic polarization curve for Sol. 1 for 1hr and Sol. 2. From the graph it can be seen that for Sol. 1 all the zones are well defined unlike Sol. 2. For Sol. 1 the active zone is which the steel bar is very resistant to the current density, which means there no effect on the passive layer around the steel. The passive zone is well defined as the steel bar starts to resist the corrosion from current density between 10^{-3} to 10^{-2} mA/cm^2 and the passive layer starts to deplete between 10^{-2} to 10^{-1} mA/cm^2 of current density and does enter into the pitting zone afterwards.

Sol. 2 which consists of Sol. 1 bubbled with CO_2 gas and with 3.5% of NaCl , the graph did not show any defined zones. The initiation of active zone for Sol. 2, started at a very low potential when compared to Sol. 1. The passive zone which is the propagation period is small or does not

existed as the passive layer was not present. It was depleted at very low potential or we can say steel didn't prepared any passive layer as there was reduction in the pH of the solution. From comparing the both samples it can be said that CO_2 along with NaCl in the solution causes rapid deterioration of the steel bar due to carbonation and chloride induced corrosion. For the experiments different corrosion inhibitor were added to the Sol. 2 to prevent corrosion and even understand their effectiveness.

For better understanding of corrosion inhibition behaviour with respect to immersion time, Tafel plots from ACM field machine are discussed for all the specimens. Tafel plot gives variation of potential (mV) at Y-axis with respect to current density (mA/cm^2) at X-axis. Tafel plots give more precise values of Icorr and corrosion rate by the use of Tafel extrapolation. Tafel ruler function in sequencer of ACM field machine can be used for Tafel extrapolation. Tafel rulers can only be used on potential vs current graphs where the current axis is logarithmic. Three rulers are placed on the graph, a horizontal ruler which identifies the rest potential. The other rulers indicate Tafel slopes.

In order to compare the performance of chemicals as corrosion inhibitors, Tafel plots of the specimens immersed in these chemicals are compared with the Tafel plot of the specimen immersed in carbonated calcium hydroxide solution with NaCl (Sol. 2).

Corrosion current density values less than 10^{-4} mA/cm^2 correspond to passive condition and corrosion current density values ranging between 10^{-4} mA/cm^2 and 10^{-3} mA/cm^2 correspond to moderate corrosion rate. Similarly corrosion current density values ranging between 10^{-3} mA/cm^2 and 10^{-2} mA/cm^2 and between 10^{-2} mA/cm^2 and 10^{-1} mA/cm^2 correspond to high and very high corrosion rate respectively *(M.Moreno et al., 2004)*.

5.3 TEST RESULTS OF VARIOUS SPECIMENS AT DIFFERENT IMMERSION TIMES

A total of 36 steel specimens were tested, and for each of the steel specimen a new solution was prepared every time, because after testing the solutions had the residuals of the respective steel bar and were not fit to be tested again.

The passive films formed under these conditions consist of species such as $Fe(OH)_2$, $Fe(OH)_3$, and Fe_3O_4, which are chemically stable species under the pH and potential conditions established.

For comparing the effectiveness of chemical corrosion inhibitors, the readings were obtained from Current and Voltage per time and LPR sweep tests, and these readings were compared according to the time intervals.

5.3.1 After 1 Hour

After preparing steel specimens and submerging them partially in the respective solutions for a time of 1 hour, two tests were performed on each specimen i.e. Half-Cell potential or last rest potential (Rp) & LPR sweep, through which following results have been obtained.

The results obtained after a time of 1 hour were not much dependable as the time provided to inhibitors to prove their inhibiting qualities was not sufficient. Table 5.3 shows the Half-Cell potential readings and Icorr results after 1 hour of immersion.

Table 5.3 Half-Cell potential and Icorr results after 1 hour of immersion

Sol. No.	Rp (-mV)	Icorr (mA/cm^2)
Sol. 1	390.5	0.057
Sol. 2	661	1.175
Sol. 3	655	1.323
Sol. 4	545	1.315
Sol. 5	663	1.031
Sol. 6	543	0.41

The difference between the half-cell potential is clearly visible, as for Sol.1 the value was -390mV and for rest of the solutions the value of HCP was in zone of severe corrosion. These values gives us an idea about the high probability of corrosion in the other specimens, and is generally due to the presence of chlorides and the carbonated nature of the solution.

The curve obtained from the LPR sweep tests of all the solutions after 1 hour, clearly shows that except 4-Aminobenzoic acid all of the inhibitor have shown their inhibiting quality. An active region, where the current density was lower than 10^{-3} mA/cm^2, was observed in the controlled specimen (Sol. 1) before the starting of breaking of passive layer. The major difference was a

displacement of the curve towards lower potentials that was associated to the lower pH of the carbonated $Ca(OH)_2$ solution and the presence of Cl^- ions.

From the Figure 5.3 it is also clear that the steel specimen in Sol.1 had shown presence of passive layer formation, whereas in the rest of the solutions no presence of passive layer was seen. The readings of HCP and corrosion current density were very high for all specimens having corrosion inhibitors except 4-Aminobenzoic Acid (Sol.6). So, initially it was thought that these set of corrosion inhibitors are not effective in carbonation and chloride induced corrosion.

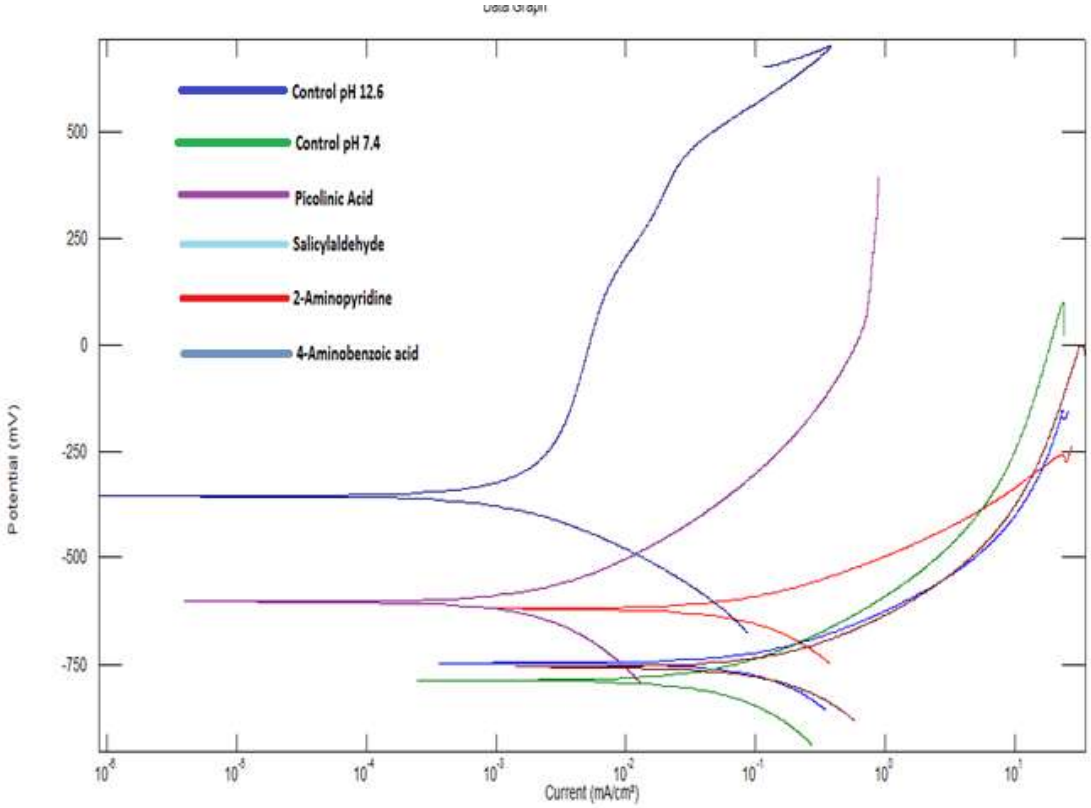


Figure 5.3 Tafel plot for various solutions immersed for 1 hour

5.3.2 After 24 Hours of immersion

After preparing steel specimens and placing them in the respective control and chemical inhibitor solutions for a time of 24 hours, two tests were performed on each specimen i.e. Half-Cell Potential & LPR sweep, through which following results have been obtained.

Table 5.4 Half-Cell potential and Icorr results after 24 hour of immersion

Sol. No.	Rp (-mV)	Icorr (mA/cm^2)
Sol. 1	472.5	0.04
Sol. 2	711.1	1.275
Sol. 3	588.5	1.204
Sol. 4	660.1	1.118
Sol. 5	656.2	1.175
Sol. 6	544.2	0.525

From the values of half-cell potential and Icorr From Table 5.4, it can be seen that the control solution with pH 7.4 without any corrosion inhibitor (Sol. 2), have half-cell potential of -711mV which clearly depicts that there wasn't any presence of passive layer, which results in initiation of corrosion. From the values obtained of Icorr and last rest potential it was clear that the inhibitors were forming a passive layer around the steel specimen and hence started working as compared to control Sol. 2.

The Icorr Value for 4-Aminobenzoic Acid is $0.525mA/cm^2$ which gives us an idea that in the initial stages 4-Aminobenzoic acid has performed exceptionally well as compared to the other corrosion inhibitors. Along with it, Salicylaldehyde has also performed well as compared to other inhibitors.

In order to compare the performance of chemicals as corrosion inhibitors, Tafel plots of the specimens immersed in these chemicals were also compared with the Tafel plot of the specimen immersed in carbonated calcium hydroxide solution (Sol. 1). The comparison of Tafel plots is shown in Figure 5.4.

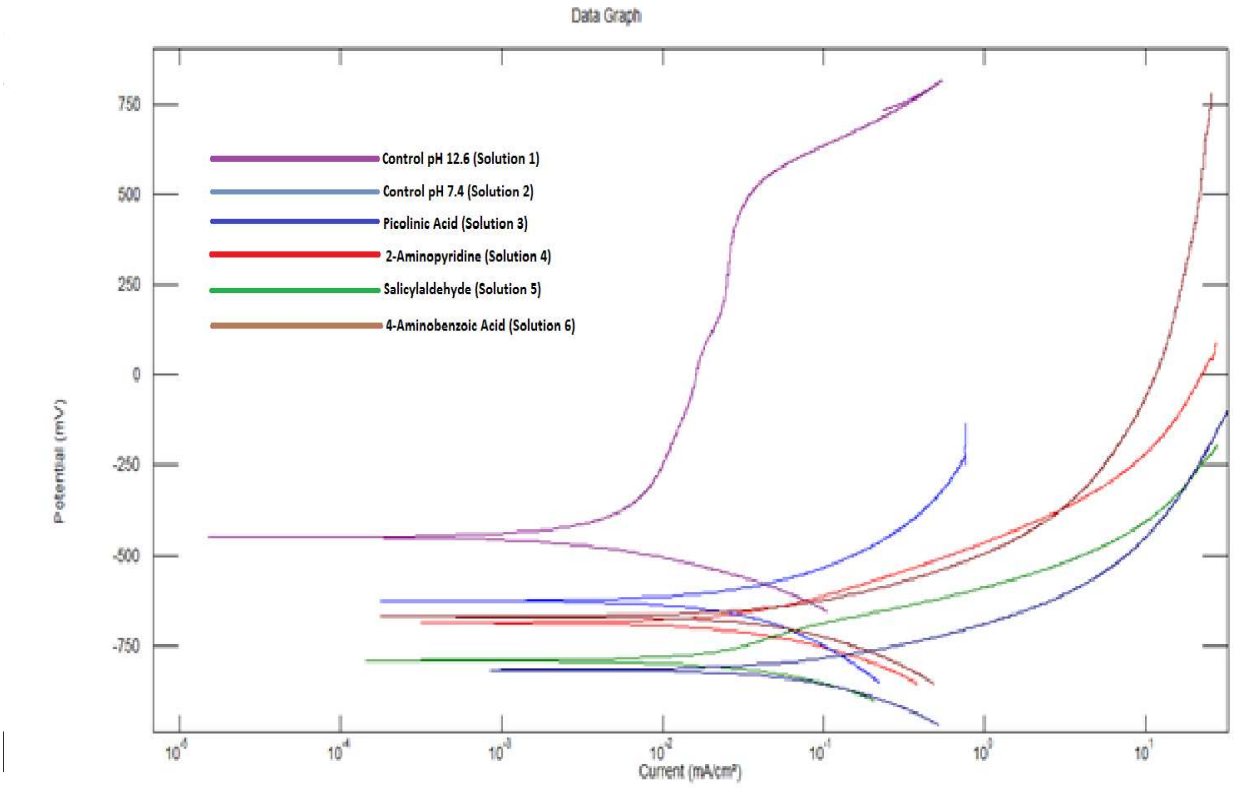


Figure 5.4 Tafel plot for various solutions immersed for 24 hour

As can be observed from the Fig. 5.4, in Sol. 1 (saturated Ca(OH)2 having pH 12.1) steel shows a current density of 10^{-2} mA/cm^2 with passive behaviour up to 10^{-1} mA/cm^2 while in Sol. 2 the corrosion potential shifts towards the active zone with Icorr value of 10^{0} mA/cm^2 and no explicit passive behavior was observed after 24 hours of immersion. All the other solution having chemical corrosion inhibitors i.e. Sol 3,4,5,6 were able to perform marginally as compared to Sol. 2.

5.3.3 Test results after a time period of 48 hour

After preparing steel specimens and placing them in the respective control solutions and chemical inhibitor solutions for a time of 24 hours, two tests were performed on each specimen i.e. Half-Cell Potential & LPR sweep, through which following results have been obtained.

The results of last rest potential and Icorr obtained by performing tests are given in Table 5.5.

Table 5.5 Half-Cell potential and Icorr results after 48 hour of immersion

Sol. No.	Rp (-mV)	Icorr (mA/cm^2)
Sol. 1	491.78	0.045
Sol. 2	732.2	2.551
Sol. 3	648.30	1.841
Sol. 4	639.1	1.85
Sol. 5	680.2	1.12
Sol. 6	560	0.783

The values of Icorr and Rest potential obtained depicts that the specimen which was in Sol. 1 showed noble passive behaviour till 48 hours of immersion. A shift of Icorr value towards higher corrosion was observed after 48 hours of immersion in Sol. 1, whereas the specimens in all the solutions with inhibitors showed a huge rise in Icorr value, which clearly depict that even after 48 hours of immersion time all the corrosion that has been formed on the surface of steel bar will disintegrate and will expose the layer beneath it to the respective solution.

Picolinic Acid along with 2-Aminopyridine proved to the worst inhibitor for a short period of time (upto 48 hours) as the values of Icorr was maximum for them i.e.1.841mA/cm^2 and 1.85 mA/cm^2 respectively, whereas 4-Aminobenzoic Acid was the best among them with an Icorr value of 0.783 mA/cm^2.

Tafel plot of specimen immersed in Sol. 6 (4-Aminobenzoic Acid) shown in Fig. 5.5 depicted that the HCP for this specimen had shifted to a lesser value, which further showed a shift towards passive zone after 48 hours of immersion. Small shift towards active zone at 48 hours of immersion was observed for Sol. 1. No passive behaviour was observed till 48 hours of immersion for Sol. 3 (Picolinic Acid), Sol. 4 (2-Aminopyridine) and Sol. 5 (Salicylaldehyde) respectively.

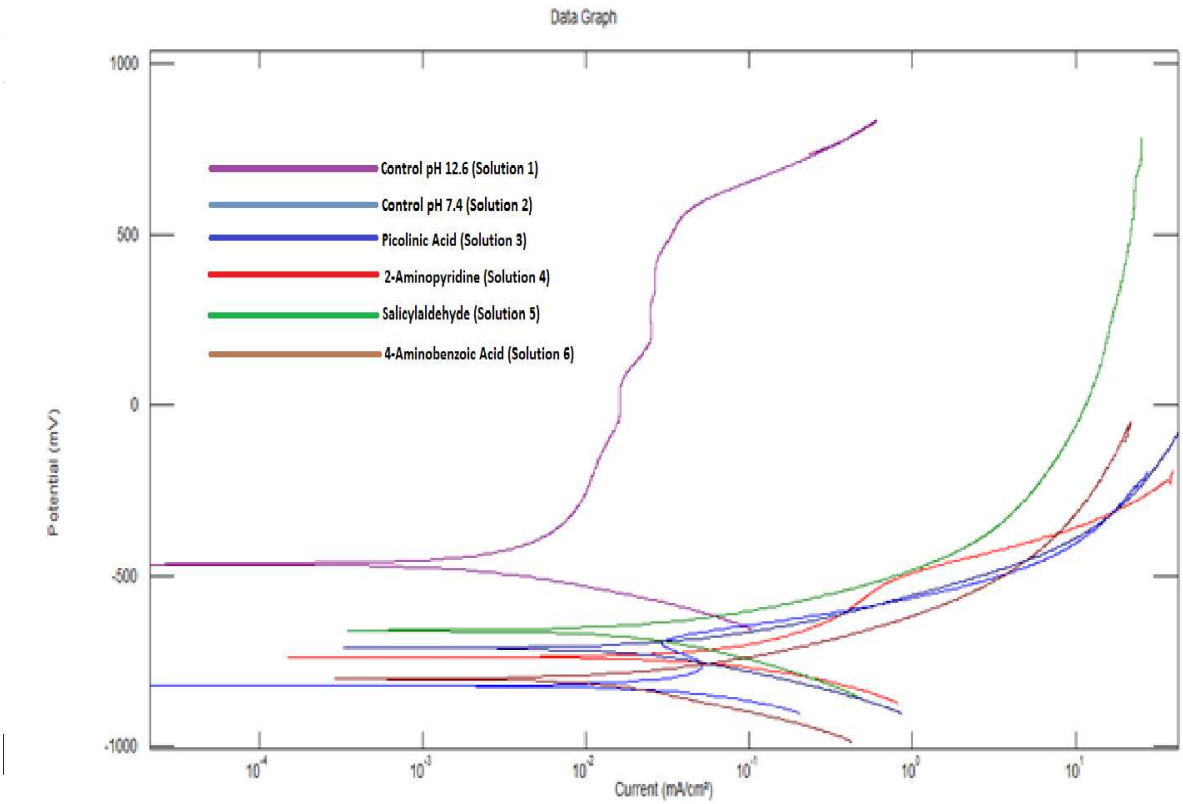


Figure 5.5 Tafel plot for various solutions immersed for 48 hour

Hence through these polarization curves it can be concluded that after 48 hours of immersion except 4-Aminobenzoic acid, none of the chemical inhibitor has shown any remarkable progress in achieving passivation. All the specimen with corrosion inhibitors were having a rest potential of less than -600mV.

5.3.4 Test results after 120 hours of immersion

After the steel specimens being immersed partially in the respective solutions for a period of 120 hours, Half-cell potential and LPR sweep tests were performed on each sample. The time provided before the tests were conducted was sufficient for the chemical corrosion inhibitors, to show their partial efficiencies. When the results were compared with the control specimen i.e. Sol. 2, every sample containing corrosion inhibitor (i.e. Sol. 3, Sol. 4, Sol. 5, Sol.6) performed well. The results obtained from HCP and LPR sweep test are given in Table 5.6.

Table 5.6 Half-Cell potential and Icorr results after 120 hour of immersion

Sol. No.	Rp (-mV)	Icorr (mA/cm^2)
Sol. 1	705.5	0.38
Sol. 2	746.2	2.355
Sol. 3	674.6	1.751
Sol. 4	653.78	1.283
Sol. 5	649.5	1.552
Sol. 6	597.9	1.475

Through the values obtained of Icorr and Half-cell potential, it can be seen that the control specimen with pH 12.6 (Sol. 1) is now probable to corrode. 4-Aminobenzoic acid which has shown very promising nature earlier has declined its performance.

Although just on the readings obatined from Half-cell potential it can't be concluded that which of the chemical corrosion inhibitor has perfomed best. Therefore LPR test was also conducted on the same sample for having more information about the respective sample.

Tafel plots of specimens immersed partially after a period of 120 hours is shown in Figure 5.6.

As it can be observed from Tafel plot of specimen in Sol. 1 shown in Fig. 5.6, Icorr value shifts toward active zone showing no passive behaviour with increasing immersion time. Icorr value for this specimen was 0.057mA/cm2 at 1 hour of immersion which shifted to 0.38 mA/cm2 at 120 hours.

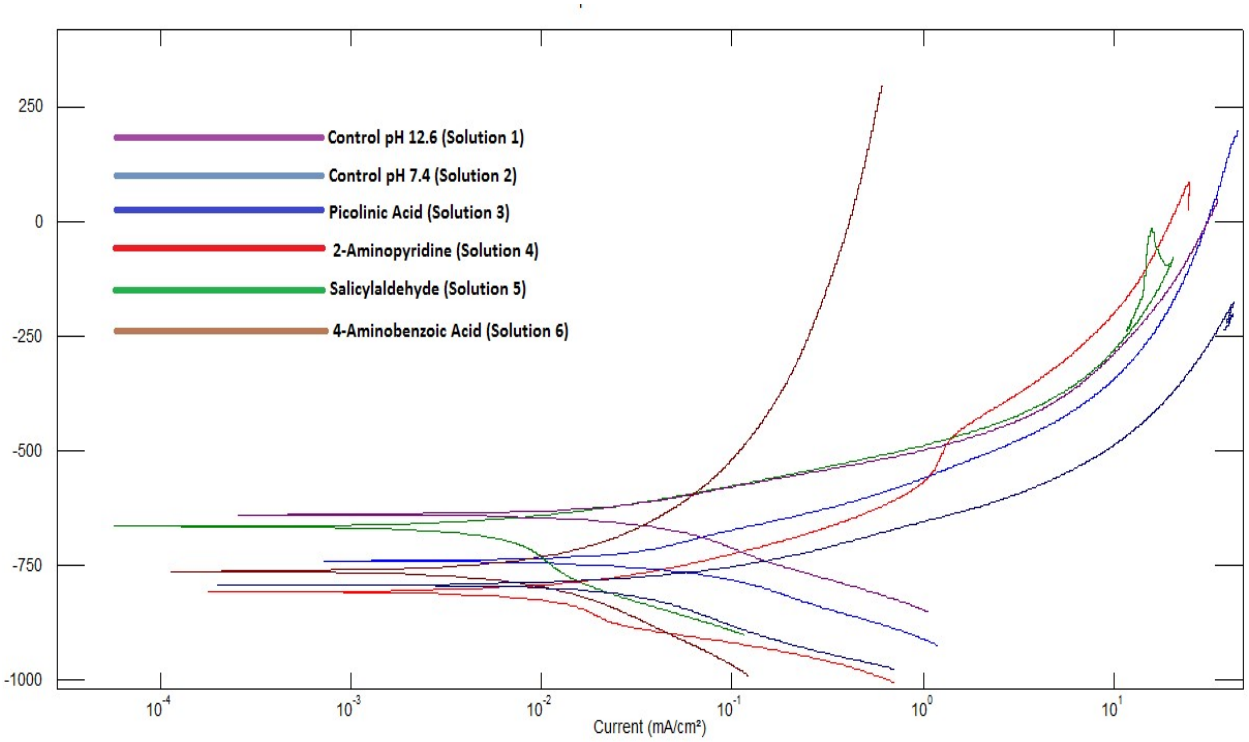


Figure 5.6 Tafel plots for various solutions immersed for 120 hour

By the values obtained from LPR sweep test it can also be concluded that after a time period of 120 hours all the chemical corrosion inhibitors have approximately the same efficiencies.

After 120 hours there was a visible difference that can be seen with naked eyes, between the appearances of steel specimens that were just tested. After the tests were performed the steel specimens were thoroughly inspected and it was found that a passive layer has started to form on all the steel specimens, those were in Sol. 3, Sol. 4, Sol. 5 and Sol. 6. Whereas the steel specimen which was in Sol. 2 has started to corrode severely.

The physical appearances of different steel specimen after 120 hours of partial immersion is shown in Figure 5.7.

It can be seen that the specimen which was immersed in Sol. 2 has a large amount of corrosion products on it. As the volume of corrosion rust is 3-6 times as iron *(Tommaselli, 2009*), it can be seen in the figure that the volume expansion has caused cracking of the epoxy.

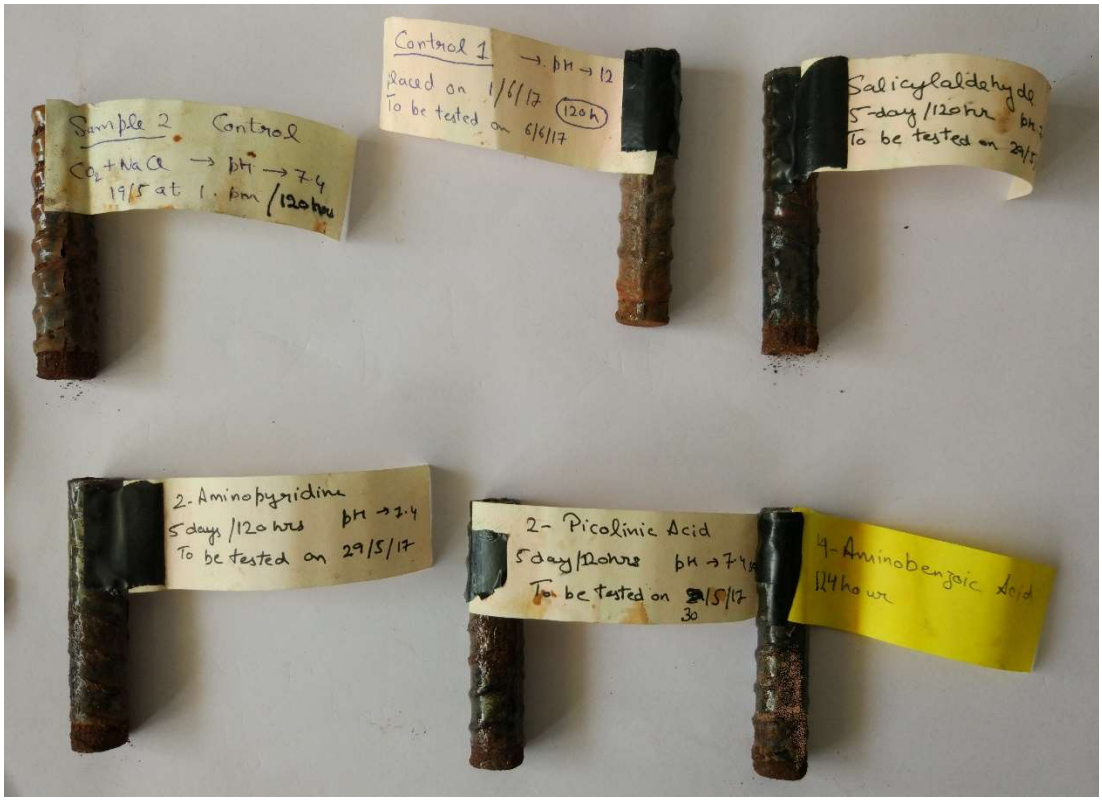


Figure 5.7 Steel specimens after measuring Half-cell Potential and Linear Polarization Resistance, immersed partially in different solutions after 120 hours

When compared to other specimens, it is clearly shown that at 120 hours of partial immersion in corrosion inhibitor, all the inhibitors are working with approximately equal effectiveness up to this point with 2-aminopyridine showing a higher amount of resistance to corrosion.

The specimen in solution containing Salicylaldehyde (Sol. 4) may seems to have lesser rust on it but when the LPR Sweep was performed for this sample it was found that the corrosion was present on it.

Therefore after 120 hours it can be concluded that the chemical corrosion inhibitors has started to form a passive layer on the steel surface, which results in resisting the corrosion, as compared to the control specimen in Sol. 2.

5.3.5 Test results after 240 hours of immersion

The results obtained after a time period of 120 hours showed that chemical corrosion inhibitors had shown their partial efficiencies. Therefore to obtain a more clear view about the efficiencies of respective inhibitors a test was also conducted after 240 hours.

Table 5.7 Half-Cell potential and Icorr results after 240 hour of immersion

Sol. No.	Rp (-mV)	Icorr (mA/cm^2)
Sol. 1	743.5	0.0255
Sol. 2	738.08	2.276
Sol. 3	665.2	0.77
Sol. 4	496.8	0.768
Sol. 5	700	1.049
Sol. 6	692.2	1.185

The values obtained of rest potential and Icorr was a clear proof that all the corrosion inbitors have inhibited a specific amout of corrosion as compared to the control Sol. 2. Table 5.7 clearly shows the difference in the values of current densities of control specimen (Sol. 2) i.e. 2.276 mA/cm2 which depicts a high corrosion density, when compared to Sol. 1 which is at 0.0255 mA/cm2.

Figure 5.8 compares the tafel plot for different chemical inhibitors with control solutions after a time period of 240 hours. After 240 hours the values obtained from half-cell potential were not so promising as the value of HCP for Sol. 1 was -743 mV which was equal to the value of HCP obtained for Sol. 2. But after obtaining results from LPR sweep test and by inspecting the specimens with naked eyes it could be definitely proven that corrosion on the specimen in Sol. 2 is severe, whereas the corrosion on specimen from Sol. 1 is in starting stages.

Therefore it can be concluded that although the values of HCP tests for Sol. 1 and Sol. 2 are almost equal, but the specimen from Sol. 1 is still resisting to corrosion.

To obtain more clearity tafel plots of all the solutions after 240 hours were compared and is shown in Figure5.8.

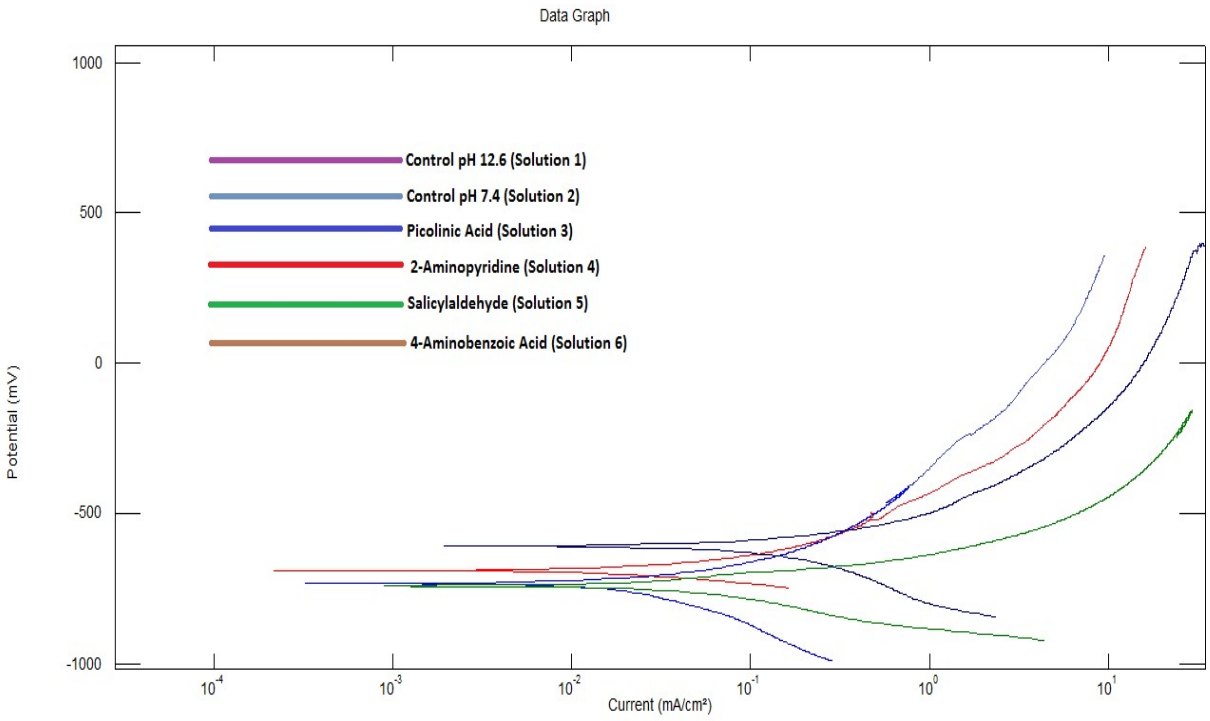


Figure 5.8 Tafel plot for various solutions immersed for 240 hours

Figure 5.9 Steel specimens after measuring Half-cell Potential and Linear Polarization Resistance, immersed in different solutions after 240 hours

Figure 5.9 shows the physical appearances of different specimens submerged partially in different solutions for a period of 240 hours.

From the Figure 5.8 and Figure 5.9, it is clearly visible that the corrosion in control specimen (Sol. 2) is so severe that even the epoxy layer on the surface has started disintegrating.

In solutions where only carbonation is present, epoxy holds for a longer period of time but in the presence of chlorides epoxy didn't hold for a long period of time under chloride attack *(McHattie JS 1996)*. From the Icorr values obtained it can be concluded that 2-Aminopyridine has performed best among all the inhibitors followed by 4-Aminobenzoic acid.

5.3.6 Test results after 480 hours of immersion

For obtaining a long term effectiveness of chemical corrosion inhibitors, specimens were tested in each solution for a time period of 480 hours. After 480 hours the control specimen in Sol. 2 has completely corroded and was left of no use, as the rust formed on its surface had reached up to a depth of 2mm.

Table 5.8 Half-Cell potential and Icorr results after 480 hour of immersion

Sol. No.	Rp (-mV)	Icorr (mA/cm^2)
Sol. 1	769.21	0.032
Sol. 2	739.2	2.030
Sol. 3	595.2	0.085
Sol. 4	400.5	0.179
Sol. 5	577	0.033
Sol. 6	568	0.058

The values of HCP and Icorr are showing variations from the start, and after a time of 480 hours the value of Icorr is very low as acompared to the control sample with ph=7.4 (Sol. 2), which indicates that all the chemical corrosion inhibitors were efficient in resisting corrosion.

There were some variations in the results among the inhibitors itself, which shows that 2-Aminopyridine has performed best among all the inhibitors followed by salicylaldehyde.

Figure 5.10 Steel specimens after measuring Half-cell Potential and Linear Polarization Resistance, immersed in different solutions after 480 hours

Figure 5.10 shows the physical appearance of steel specimens which were tested in their respective solutions. From the figure above it can be concluded that each of the inhibitors have shown significant amount of inhibition as compared to the control specimen of ph=7.4 (Sol. 2). The specimen in Sol. 2 has been corroded severely, all the steel part that has been exposed has corroded, and rust is falling off from the surface. This is due to the fact that throughout the time period passive layer wasn't formed on the surface, resulting in continuous exposure of steel layer to the corroding environment around it.

To compare the results tafel plots of the different corrosion inhibitors is compared in the Figure5.11.

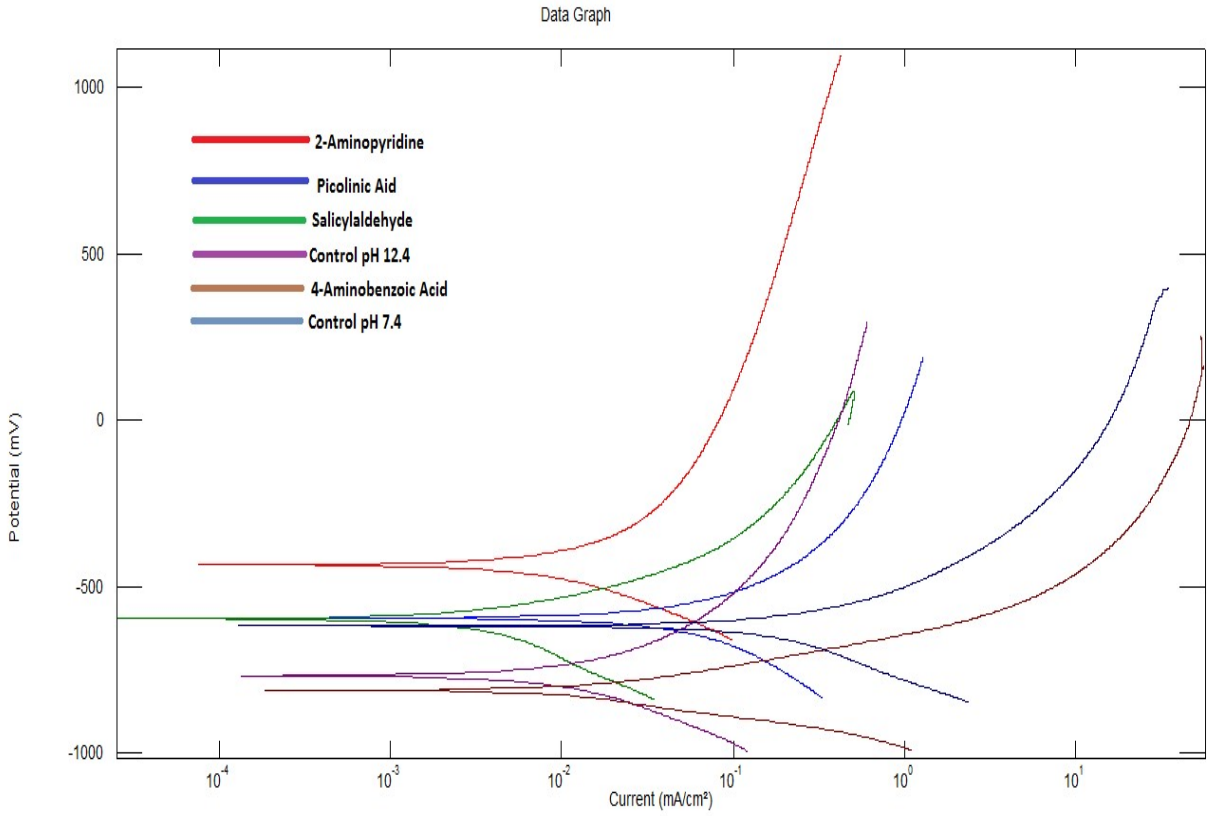


Figure 5.11 Tafel plot for various solutions immersed for 480 hour

Through the tafel graph obtained of each chemical inhibitor (Sol. 3, Sol. 4, Sol. 5, Sol.6), it can be concluded that each chemical corrosion inhibitor has performed as expected.

5.4 CHEMISTRY BETWEEN CORROSION INHIBITOR AND STEEL SURFACE

The reason for the chemicals acted as a barrier for corrosion can be explained considering the chemistry between corrosion inhibitor and concrete. Two types of chemical bonds were formed in order to form a passive layer around the bare steel surface, one when the amine part in the chemical inhibitor bonded with the metal and other when the hydroxide group part in the inhibitor got linked with metal.

Amine based corrosion inhibitor is said to be chelating agent, which can form five or six membered chelate rings (groups which function as two associating units and fasten on to the central metallic atom so as to produce heterocyclic rings). Figure 5.12 shows the way through which the amine based corrosion inhibitors has formed chelated rings around steel bars.

Figure 5.12 Chelating ring formed around metal bar

These rings are formed as a result of bonding between two or more functional groups from the inhibitor (-NH2) and the cation metal. Due to the presence of rings, Amine organic inhibitors have film-forming effects. The film-forming component is an amine group. They get adsorbed on metals and oxides because of an unshared electron pair of the nitrogen atom. *Welle et al. (1997)* and *Nmai (2004)* report that amines and the associated radicals form a layer on the steel surface which completely cover all the anodic and cathodic sites. The film forming effect, therefore depends on the property of corrosion inhibitor and does not depend upon the quality of concrete. *Jamil et al. (2003)* further observed that the thickness and composition of the protective film depends on the concentration of inhibitor. The limit concentration of inhibitor to form the protective film is reported to be 0.5 – 1%. Further, it is observed that higher concentration of inhibitor (2% to 4%) does not have any effect on the protective film *Jamil et al. (2005)*.

The typical passive layer formation chemistry of individual chemical as corrosion inhibitor is discussed in the following sections.

5.4.1 Chemistry between 2-Aminopyridine and Steel surface

2-Aminopyridine is an organic compound with the formula $H_2NC_5H_4N$. Figure 5.13 shows the chemical formation of chelated ring around the steel surface.

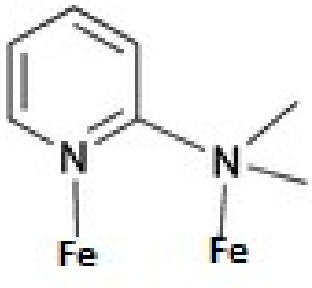


Figure 5.13 Chelated ring formed by 2-Aminopyridine around steel

As 2-Aminopyridine consists of 2 nitrogen atoms, and both of them makes bond with the steel surface, hence forms a passive layer on the steel surface which completely cover all the anodic and cathodic sites.

5.4.2 Chemistry between 4-Aminobenzoic Acid and Steel surface

4-Aminobenzoic acid (also known as para-aminobenzoic acid or PABA because the number 4 carbon in the benzene ring is also known as the para position) is an organic compound with the formula $H_2NC_6H_4CO_2H$.

Figure 5.14 shows the chemical composition of passive layer that has been formed around steel bar after submerging partially in Sol. 6.

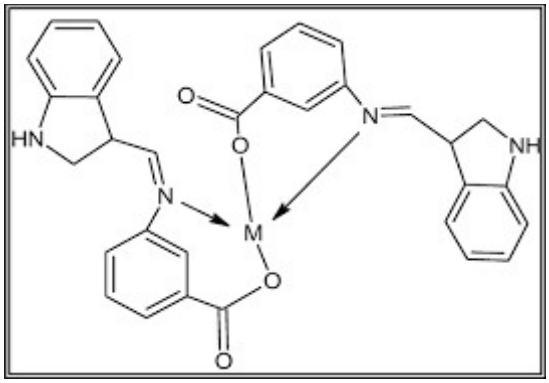


Figure 5.14 Chelated ring formed by 4-Aminobenzoic Acid around steel

5.4.3 Chemistry between Picolinic Acid and Steel surface

Picolinic acid is an organic compound with the formula $C_5H_4N(CO_2H)$. It is a derivative of pyridine with a carboxylic acid substituent at the 2-position. Corrosion properties of picolinic acid is due to the partial covalent bonds it forms with the metal.

Figure 5.15 shows the partial bonds in which each hydroxide present on the benzene loses its hydrogen atom and forms a partial bond with the metal in between, during this process the oxygen atom attains a negative charge.

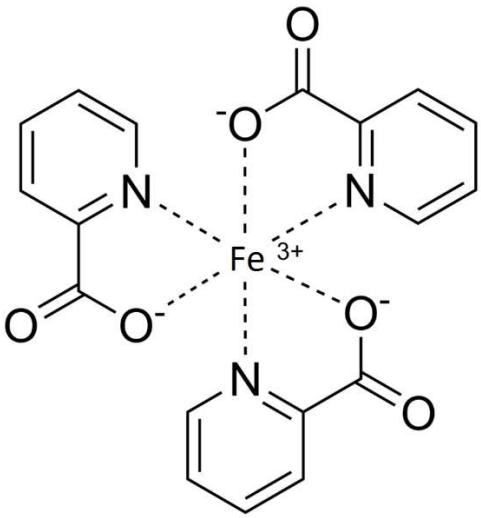


Figure 5.15 Chelated ring formed by Picolinic Acid around steel

5.4.4 Chemistry between Salicylaldehyde and Steel surface

Salicylaldehyde (2-hydroxybenzaldehyde) is the organic compound with the formula C_6H_4CHO-2-OH. This colorless oily liquid has a bitter almond odour at higher concentration. Like the other chemical corrosion inhibitors salicylaldehyde doesn't contain any amine group. Although it also helps in providing a barrier against corrosion by forming a passive layer around steel, but it uses its oxygen atom in order to form a passive layer.

The chemical bond it shares with metal required for passivation is shown in Figure 5.16.

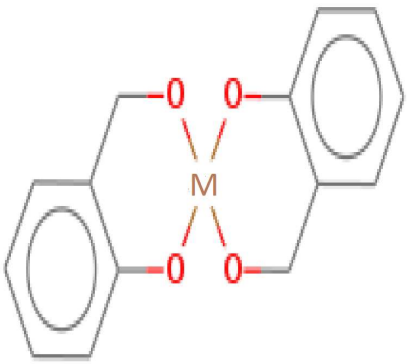


Figure 5.16 Chelated ring formed by Salicylaldehyde around steel

5.5 COMPARISONS OF ALL THE INHIBITORS WITH CONTROL SOLUTIONS

To compare the different efficiencies of various chemical corrosion inhibitors mainly two tests were performed on each solution, Half-cell potential and LPR sweep respectively.

5.5.1 Half-Cell potentials vs Time

The Half-Cell potential readings just indicate the de-passivation of steel and hence the possibility of corrosion. This gives a rough idea of whether the corrosion has started or not. The results obtained by only Half-cell potential were not much dependable. According to ASTM standards the Half-Cell potential below -250 mV shows that the corrosion has not yet started. Figure 5.17 shows the comparison of HCP readings obtained by the different solutions at different time intervals.

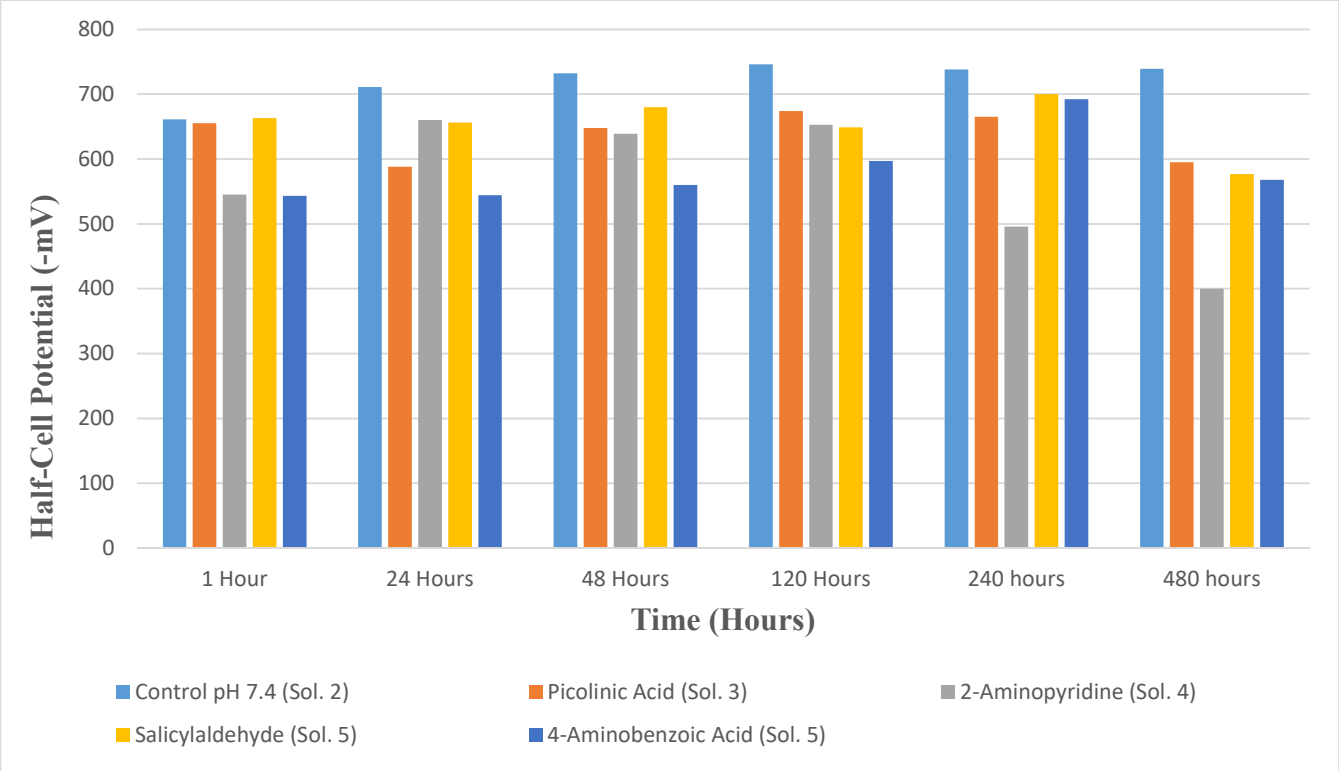


Figure 5.17 Variation of Half-cell potential (-mV) vs Time

The graph of HCP vs immersion time depicts the following:

- The value of half-cell potential for Sol. 2 i.e. control solution of pH 7.4 is varying between 650-800mV which proves that the probability of corrosion is above 90% throughout,

irrespective of the time variation. Similar observations of high Half-Cell potentialin pore solutions was made by *R. Liu et al. (2014).*

- The values of Half-Cell potentialobtained for Sol. 1 was not according to the ASTM C 876 – 91, as according to ASTM standards, below -426mV there is 90% probability of corrosion. But the actual amount of corrosion was not according to the results. This is due to fact that ASTM C876-91 is only for concrete and not for pore solutions simulating environment of concrete. Similar results were also obtained by *R. Liu et al. (2014), Tommaselli et al. (2009)* and various other researchers.
- The half-cell potential of 2-Aminopyridine (Sol. 4) was -400mV after 480 hours, when compared to the readings obtained by other solutions of corrosion inhibitors, it can be concluded that 2-Aminopyridine has the best Half-cell potential.
- The half-cell potential of Picolinic Acid did not vary much, as it remained around -600mV, which will keep a probability of corrosion.
- Half-cell potential of 4-Aminobenzoic acid has decreased up to an immersion time of 240 hours but after that it has shown a decrement of -125mV, which proves that 4-Amiobenzoic acid has prepared it passive layer earlier than the other inhibitors but at a later stage its performance has decreased.

5.5.2 $Icorr_{osion}$ (mA/cm^2) vs Time (hours)

Corrosion initiation described as the process by which chloride ions accumulate around the reinforcing steel, thereby breaking down passivity of the reinforcing steel and allowing corrosion to initiate. Corrosion propagation is described as the process by which the rate of corrosion is accelerated by the electric current at a constant voltage. Half-cell potential is effective only in monitoring the corrosion initiation. Therefore, LPR measurements are necessary as the values obtained from corrosion current density indicate the progression of corrosion in the propagation phase. The LPR readings were taken along with the Half-Cell potential readings of each specimen.

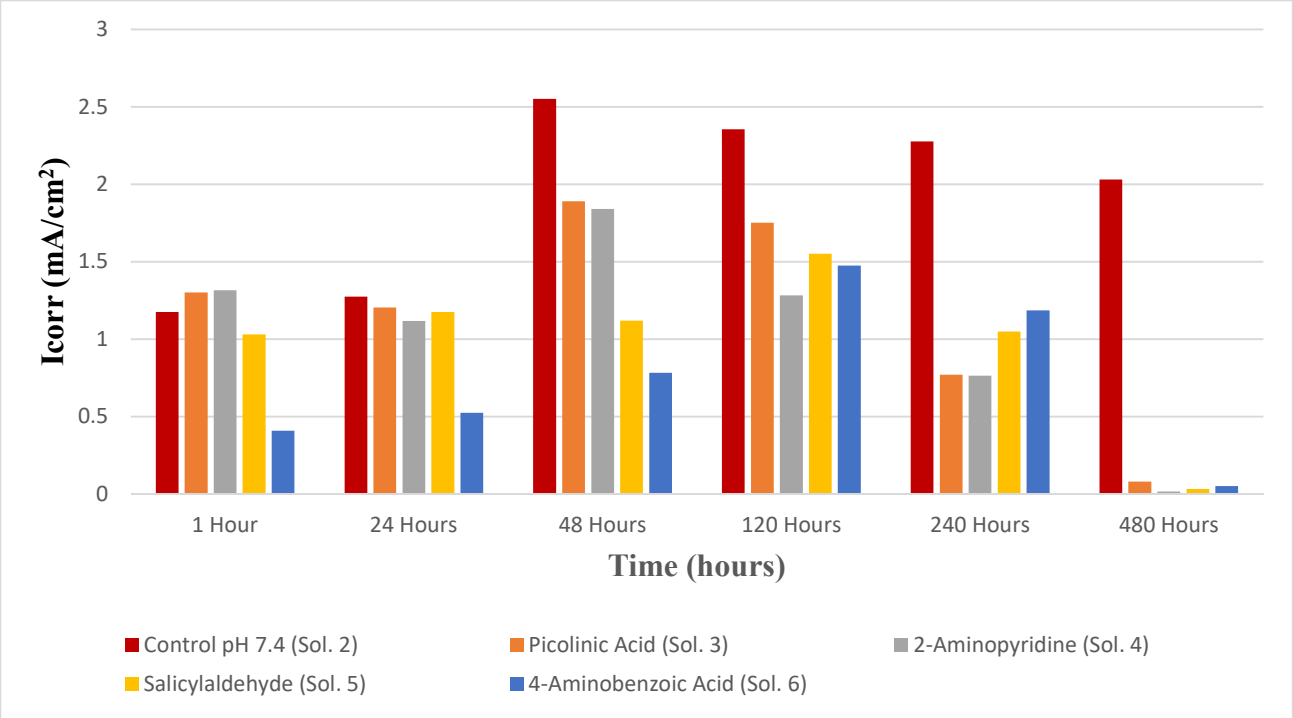


Figure 5.18 Variation of Icorr (mA/cm^2) vs Time

The graph of Icorr$_{osion}$(mA/cm^2) vs Immersion time(hours) for all pore solutions is presented in Figure 5.18, the following observations can be seen from the graph.

- A general trend of forming a passive layer around steel surface after 240 hours of immersion, among all the corrosion inhibitors can be observed due to the fall in Icorr values after 240 hours.
- At 48 hours of immersion Sol. 2 (control solution of pH 7.4) showed maximum value of Icorr i.e. 2.55mA/cm^2.
- At earlier stages 4-Aminobenzoic acid (Sol. 6) performed better as compared to other corrosion inhibitor, but after 120 hours its performance started declining. Hence it can be understood that 4-Aminobenzoic acid (Sol. 6) provided proper inhibition due to the early passive layer formation.
- Whereas 2-Aminopyridine (Sol. 4) may not have performed as well as 4-Aminobenzoic Acid (Sol. 6) upto 48 hours of immersion but after that the reduction in the values of Icorr was maximum for 2-Aminopyridine (Sol. 4) among all the inhibitors.

- Picolinic acid (Sol. 3) and salicylaldehyde (Sol. 5) had same approach towards Icorr i.e. they both reduced the values of Icorr but were less effective from 4-Aminobenzoic acid (Sol. 6) and 2-Aminopyridine (Sol. 4).

CHAPTER 6 CONCLUSIONS

A corrosion inhibitor is a chemical substance that decreases the corrosion rate when present in the corrosion system. The principle of inhibitors is to develop a thin layer, usually one or two molecules thick, on the steel surface, which inhibits corrosion either by forming a protective film on the substrate, or by immobilizing the corrosive species and preventing them from reaching the steel.

The present study focuses on protective film forming capabilities of different chemical corrosion inhibitors. That is why the tests are performed on pore solution rather than on concrete.
From the research done for the study of effectiveness of organic chemicals as corrosion inhibitors in saturated calcium hydroxide solution with reduced alkalinity, following conclusions can be drawn:

- All the inhibitors have proven themselves in inhibiting the carbonation and chloride induced corrosion by forming a passive layer on the steel surface.
- Both electrochemical techniques are good for measurement of corrosion rate. Linear polarization method gives better results than Half-Cell potential measurement because half-cell potential gives only the indication of de-passivation. From the determined corrosion current density values by LPR method, it is concluded that effect of significant reduction in corrosion risk is observed effectively by linear polarization resistance measurements.
- The values of Half-cell potential and Icorr standardized by ASTM C 876-91 are for concrete only and not for pore solutions. Therefore relatively higher values obtained for HCP and Icorr in this study are justified. This is also validated by other researchers.
- Up to a time of 48 hours Icorr and half-cell potential has shown an increasing trend, but after that inhibitors came into action and the values of Icorr and half-cell potential has started declining.
- 2-Aminopyridine has proven itself a very effective corrosion inhibitor of steel bar when mixed in carbonated calcium hydroxide solution with reduced alkalinity in the presence of NaCl, because it has two amine groups which makes bond with the metal.

- 4-Aminobenzoic acid (Sol.6) has performed well initially (at 48 hours of immersion), due to the early passive layer formation by amine group at para position, but after a time period of 120 hours the performance of all the corrosion inhibitors were similar to 4-Aminobenzoic Acid.
- After 480 hours the corrosion on control specimen with a pH of 7.4 (Sol. 2) is so absurd that the epoxy layer on the specimen has started to disintegrate.
- Picolinic acid (Sol. 3) and Salicylaldehyde (Sol. 5) both have shown a similar efficiency, lesser than 2-Aminopyridine (Sol. 4) and 4-Aminobenzoic Acid (Sol. 6) in resisting corrosion. This may be due to the fact that both of the chemicals have formed a chelated ring around steel surface by bonding their hydroxide group with the metal atom.

SCOPE OF FUTURE WORK

In this experimental research work, study of effectiveness of organic chemicals as corrosion inhibitors in saturated calcium hydroxide solution with reduced alkalinity and addition of NaCl for chlorides was performed. Performance of these chemicals at various time periods was studied.

Following the results of this research work, further investigations in this field can be performed in future. Advanced possible findings in this field are listed below:

- Performance of these chemicals in reinforced concrete can be studied by adding these chemicals in concrete mix.
- Possibility of any adverse effect of these chemicals on other concrete properties like strength, permeability etc. can be studied.
- Corrosion inhibition of these chemicals for various types of steel bars can be studied.
- Probability of any reaction of these chemicals with other admixtures like superplasticizers and air entraining agents can be studied.

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